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National Dry Deposition Network
Second Annual Progress Report (1988)

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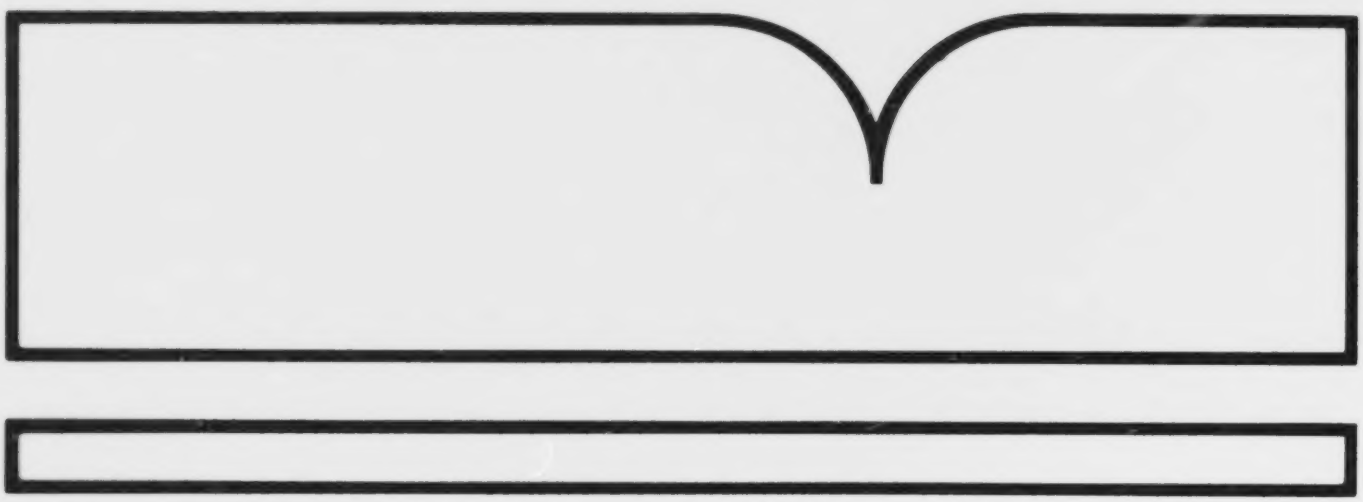

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16. ABSTRACT

Progress in the National Dry Deposition Network during calendar year 1988 is presented. The network configuration and operating procedures for the field, laboratory, and data management center are described and data are summarized. Forty-three sites were operational at the close of 1988. Each site was equipped with sensors for measuring ozone and meteorological parameters required by inferntial dry depositon algorithms, Weekly average day/night concentration of sulfate, nitrate, sulfur dioxide, and nitric acid were measured using a three-stage filter pack. Sodium, potassium, calcium, magnesium and ammonium were measured during half of the year. Ambient concentration data for 18 sites operational throughout the year showed species-dependent variability from site to site, season to season, and day to night. Average SO_4^{2-} and HNO_3 were highest during summer (10 and 3 $\mu g/m^3$, respectively) and lowest during fall (4 and 1.8 $\mu g/m^3$, respectively); SO_2 and NO_3^- highest in winter (18 and 1.7 $\mu g/m^3$, respectively)and lowest in summer (10 and 0.6 $\mu g/m^3$). Day/night variability was generally low for SO_4^{2-} and NO_3^-, but frequently pronounced for SO_2 and HNO_3. Approximations of annual dry deposition for SO_4^{2-} plus SO_2 and NO_3^- plus HNO_3 suggest that fluxes are of the same order of magnitude as wet deposition at numerous sites. Application of one or more dry depositon algorithms is needed to refine such estimtes. Examination of ozone data showed numerous observations above 100 ppb mainly associated with stagnating high pressure.

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NATIONAL DRY DEPOSITION NETWORK
SECOND ANNUAL PROGRESS REPORT (1988)

by

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FOREWORD

The Atmospheric Research and Exposure Assessment Laboratory (AREAL) is committed to performing research and development in the characterization of air pollutant sources, sinks, transport, and transformations, in the assessment and prediction of exposure of humans and ecosystems to environmental pollutants, and in the development of monitoring systems and other technologies to determine the status and trends in pollutant concentrations and the condition of the nation's ecosystems.

As national and international concern over acid deposition has grown, so has the need for information on spatial patterns and secular trends. Although wet deposition monitoring has been able to provide such information, it is realized that total acid deposition has both wet and dry components the latter of which has not been well defined. AREAL has supported the development of a network of dry acid deposition monitoring sites to demonstrate the feasibility of operating such a network and to provide a database of atmospheric dynamics and chemical concentrations that can be transformed to dry acid deposition quantities through the application of one or more dry deposition algorithms. Applications for the final data may include determination of spatial and temporal trends, evaluation of deposition models, refinement of mass balance estimates, and support to effects studies.

This report summarizes the second year's progress of the National Dry Deposition Network.

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ABSTRACT

Progress in the National Dry Deposition Network during calendar year 1988 is presented. The network configuration and operating procedures for the field, laboratory, and data management center are described, and data are summarized. Forty-three sites were operational at the close of 1988. Each site was equipped with sensors for measuring ozone and meteorological parameters required by inferential dry deposition algorithms. Weekly average day/night concentrations of sulfate, nitrate, sulfur dioxide, and nitric acid were measured using a three-stage filter pack. Sodium, potassium, calcium, magnesium, and ammonium were measured during half of the year. Ambient concentration data for 18 sites operational throughout the year showed species-dependent variability from site to site, season to season, and day to night. Average SO_4^{-2} and HNO_3 were highest during summer (10 and 3 $\mu g/m^3$, respectively) and lowest during fall (4 and 1.8 $\mu g/m^3$, respectively); SO_2 and NO_3^- were highest in winter (18 and 1.7 $\mu g/m^3$, respectively) and lowest in summer (10 and 0.6 $\mu g/m^3$ respectively). Day/night variability was generally low for SO_4^{-2} and NO_3^-, but frequently pronounced for SO_2 and HNO_3. Approximations of annual dry deposition for SO_4^{-2} plus SO_2 and NO_3^- plus HNO_3 suggest that fluxes are of the same order of magnitude as wet deposition at numerous sites. Application of one or more dry deposition algorithms is needed to refine such estimates. Examination of ozone data showed numerous observations above 100 ppb mainly associated with stagnating high pressure.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

cm/sec	-- centimeters per second
CVS	-- calibration verification standard
DAS	-- data acquisition system
DMC	-- data management center
EEPROM	-- electronically erasable programmable read-only memory
EPA	-- U.S. Environmental Protection Agency
eq/ha-yr	-- equivalents per hectare per year
IC	-- ion chromatography
ICAP	-- inductively coupled argon plasma
km	-- kilometer
L/min	-- liters per minute
m	-- meter
m/sec	-- meters per second
mm	-- millimeter
mmHg	-- millimeters of mercury
MFC	-- mass flow controller
NAAQS	-- National Ambient Air Quality Standard
NADP/NTN	-- National Atmospheric Deposition Program/National Trends Network
neq/m^3	-- nanoequivalents per cubic meter
NDDN	-- National Dry Deposition Network
ng/m^3	-- nanograms per cubic meter
NIST	-- National Institute of Standards and Technology
PC	-- personal computer
ppb	-- parts per billion
ppm	-- parts per million
QC	-- quality control
μL	-- microliter
$\mu g/L$	-- micrograms per liter
$\mu g/m^3$	-- micrograms per cubic meter
w/m^2	-- watts per square meter

SYMBOLS

Br	-- bromine
°C	-- degrees Celsius
Ca^{+2}	-- particulate calcium
HNO_3	-- nitric acid
K^+	-- particulate potassium
Mg^{+2}	-- particulate magnesium
Na^+	-- particulate sodium
NH_4^+	-- particulate ammonium
NH_4NO_3	-- ammonium nitrate
NO_3^-	-- particulate nitrate
O_3	-- ozone
SO_2	-- sulfur dioxide
SO_4^{-2}	-- particulate sulfate

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SECTION 1.0

INTRODUCTION

Atmospheric deposition takes place via two pathways, both of which are thought to be significant: wet deposition and dry deposition. Wet deposition is the result of precipitation events (rain, snow, etc.) which remove particles and gases from the atmosphere. Dry deposition, on the other hand, is the transfer of particles and gases to the landscape in the absence of precipitation. Wet deposition rates of acidic species across the United States have been well documented over the last 5 to 10 years, but, due to measurement difficulties, comparable information is unavailable for dry deposition rates.

Whereas the direct measurement of dry deposition can be extremely difficult, a number of investigations have recently shown that it can be reasonably inferred by coupling air quality data with routine meteorological measurements (Shieh et al., 1979; Hicks et al., 1985; Meyers and Yuen, 1987; Wesely and Lesht, 1988). Using analogies with heat and momentum flux, Shieh et al. (1979) computed aerosol and SO_2 deposition velocities as a function of land use, season, windspeed, and meteorological stability class. Results of this calculation for the eastern United States showed that deposition rates for both species were strongly dependent on windspeed, solar radiation, and the condition and type of ground cover. For example, rapidly growing vegetation was found to experience higher deposition rates than senescent vegetation, and forests generally experienced higher rates than short grass or snow. Wesely (1988) has expanded this approach to calculate deposition rates for various additional species (including HNO_3) and to use site-specific meteorological data. Seminal work on the subject of dry deposition has been performed by Hicks et al. (1985) and Hosker and Womack (1986), who developed, tested, and deployed the first field system for inferential dry deposition measurements.

In 1986, the U.S. Environmental Protection Agency (EPA) contracted with Hunter/ESE to establish and operate the National Dry Deposition Network (NDDN). The specific objective of NDDN is to obtain field data at 50 to 100 sites throughout the United States to establish patterns and trends of dry deposition. Ultimately, dry deposition fluxes will be calculated using measured air pollutant concentrations and inferred deposition velocities estimated from meteorological, land use, and site characteristic data. One or more of the inference approaches developed by Hicks et al. (1985) and Wesely (1988) will be used to estimate dry deposition velocities.

This report describes progress on the NDDN during calendar year 1988. The purpose of this report is to familiarize the reader with the general approach of NDDN and the various types of data which are being produced and reported to EPA. This report is not intended to provide a definitive analysis of the 1988 database. It describes the network configuration and deployment schedule as well as procedures developed for field operations, laboratory operations, database management, and quality control (QC). An overview of air quality and meteorological data for 1988, including QC results, is also presented. Finally, dry deposition rates are estimated for selected sites and compared with wet deposition rates. These estimates were prepared using literature values for deposition velocities (not the algorithms cited above) and, therefore, are intended only to illustrate likely ranges of deposition.

SECTION 2.0

CONCLUSIONS

A 51-station dry deposition monitoring network has been established. Forty-two sites are located in the eastern United States, and 9 sites are located in the western United States. Results to date indicate that data of sufficient quality to estimate dry deposition rates are being routinely collected. In short, a monitoring network is being deployed that will eventually provide nationwide measurements of air quality and estimates of dry deposition. The following major conclusions were derived from the 1988 database.

1. Day and night air quality samples were collected at all sites using a three-stage filter pack. Results for 18 sites, operational throughout the year, show species-dependent variability from site to site, season to season, and day to night. Annual average concentrations of atmospheric particulate sulfate (SO_4^{-2}) exhibited peak values of 7.2 to 7.5 micrograms per cubic meter ($\mu g/m^3$) (in southwestern Pennsylvania and northern West Virginia) and relatively low spatial variability relative to other measured species. Annual sulfur dioxide (SO_2) concentrations showed peak values of 21 $\mu g/m^3$ (in Pennsylvania and Tennessee) and significant spatial variability, which was presumably due to point source emissions and local meteorological factors. Annual nitric acid (HNO_3) concentrations exhibited peak values of 3.2 to 3.5 $\mu g/m^3$ (in Kentucky and Virginia) and similar spatial variability, as SO_2. Annual particulate nitrate (NO_3^-) concentrations exhibited peak values of 1.5 to 2.0 $\mu g/m^3$ (in Illinois and Indiana) and distinctly higher values in the midwest than the northeast. Examination of land use characteristics showed that the highest NO_3^- concentrations were found in agricultural areas, and the lowest concentrations were found in forested areas. Comparison of 1987 and 1988 concentration data for five sites showed no significant difference from year to year.

2. Seasonal variability was considerable for all four atmospheric constituents. Concentrations of SO_4^{-2} and HNO_3 increased deterministically at all sites and by a factor of 2-3 networkwide from winter to summer. In contrast, concentrations of NO_3^- and SO_2 decreased at all sites and by a factor of two networkwide over the same period.

3. Analysis of the water soluble component of atmospheric particulate ammonium (NH_4^+), particulate sodium (Na^+), particulate potassium (K^+), particulate calcium (Ca^{+2}), and particulate magnesium (Mg^{+2}) during the fourth quarter of 1988 showed that NH_4^+ was the dominant cation at virtually all sites, followed by Ca^{+2} and Mg^{+2}. Concentrations of NH_4^+ were appreciably higher at midwestern agricultural sites than at northeastern forested sites, suggesting a chemical association with NO_3^-. Calculation of ionic balances for atmospheric aerosol showed

good agreement for northeastern and southeastern sites, but a general excess of cations for the majority of midwestern sites.

4. Comparison of day and night concentration data for selected sites indicated that SO_2 and HNO_3 are typically found at moderately to substantially lower concentrations at night. Nocturnal depletion increased from a site in flat terrain to one in complex terrain, but was not observed for a mountaintop site in Virginia. Day/night variability of SO_4^{-2} and NO_3^- was much less than that of the reactive gases.

5. Results of continuous ozone (O_3) monitoring showed that concentrations above 100 parts per billion (ppb) were observed only during the period of May through August and that the majority of these were associated with four episodes of stagnating high pressure over the eastern United States. Examination of time series data for one such episode showed that peak concentrations were similar across a transect of sites from central Kentucky to Virginia. Average concentrations decreased from a mountaintop site to a rolling terrain site to a complex terrain site, presumably due to O_3 depletion within the nocturnal inversion layer.

6. Annual dry deposition rates for SO_4^{-2}, NO_3^-, SO_2, and HNO_3 were estimated for selected sites using average annual concentration data and assumed values for deposition velocity. Results have an uncertainty of at least 50 percent. Dry deposition for SO_2 and HNO_3 appear to be much greater than SO_4^{-2} and NO_3^-, respectively, unless estimated deposition velocities are greatly in error. Comparison of wet deposition and dry deposition of various sulfur and nitrogen species indicated that the two may be comparable over much of the eastern United States. Application of one or more inferential methods of dry deposition is expected to refine these estimates.

SECTION 3.0

NETWORK DESCRIPTION AND OPERATIONS

3.1 NETWORK DESCRIPTION

Figure 1 shows the location and status of 51 sites comprising NDDN, as of December 1988. Forty-one eastern sites and two western sites were in full operation at the end of the year. Monitoring equipment was installed and awaiting utility connection at eight sites (one eastern, seven western), all of which were scheduled for initiation by early to mid 1989. The single eastern site (111--Speedwell, TN) was selected as a replacement for the other site in eastern Tennessee (102--Oak Ridge). Site 102 was demobilized at the end of 1988 due to operational difficulties and the proximity of large sources of SO_2 and NO_x.

The names, locations, reporting dates, elevation, terrain, and land-use classifications of operational NDDN sites are listed in Table 1. Terrain and land-use information refers to a 10-kilometer (km) radius around the site and is presented to convey a sense of the setting within which each site operates. Note that site numbers are used for identification purposes only and do not correlate with order of installation or operation.

Of the sites listed in Table 1, 19 were operational during the first calendar quarter of 1988, 28 were operational during the second quarter, and 33 were operational during the third quarter. With the exception of the Georgia site (153--Georgia Station), all sites established through the first half of 1988 were located in a region bounded by the Mississippi River to the west and by Tennessee and North Carolina to the south. Deployment in this fashion assisted another EPA program designed to provide field data for evaluation of one or more regional acid deposition models (Barnes et al., 1987). Dual sets of monitoring equipment were operated at West Point, NY (i.e., Site 103/4) for the first through third quarters of 1988. The purpose of this effort was to obtain precision data for independently operated sensors.

For purposes of discussion, the eastern United States sites can be divided into three regions: midwestern, northeastern, and southeastern. The midwest includes the states of Illinois, Indiana, Kentucky, Michigan, Ohio, and Wisconsin and contains 14 NDDN sites. The southeast includes the states of Arkansas, Alabama, Georgia, Florida, Mississippi, North Carolina, and Tennessee and contains 10 sites. The northeast includes the remaining eastern states, from Virginia to Maine, and contains 17 sites. Inspection of land-use information in Table 1 shows marked regional differences in the

Figure 1. Status of NDDN monitoring sites--December 1988

TABLE 1. NDDN SITES IN OPERATION DURING 1988

Site No.	Site Name	Initial Reporting Date	Latitude	Longitude	Elevation (m)	Land Use	Terrain
101	Research Triangle Park, NC	01/06/87	35.90	78.87	94	Forested-Urban	Rolling
102	Oak Ridge, TN	01/06/87	35.96	84.29	341	Forested	Complex
103/4	West Point, NY	01/06/87	41.35	74.05	203	Forested	Complex
105	Whiteface Mountain, NY	01/06/87	44.39	73.86	622	Forested	Complex
106	PSU, PA	01/06/87	40.79	77.95	393	Agricultural	Rolling
107	Parsons, WV	01/14/88	39.09	79.66	505	Forested	Complex
108	Prince Edward, VA	11/01/87	37.17	78.31	146	Forested	Rolling
109	Woodstock, NH	12/31/88	43.94	71.70	250	Forested	Complex
110	Connecticut Hill, NY	09/14/87	42.40	76.65	515	Forested	Rolling
112	Kane Experimental Forest, PA	12/31/88	41.60	78.77	618	Forested	Rolling
113	M.K. Goddard, PA	01/08/88	41.09	80.15	384	Forested	Rolling
114	Deer Creek State Park, OH	09/30/88	39.63	82.26	265	Agricultural	Rolling
115	Ann Arbor, MI	06/30/88	42.42	83.90	267	Forested	Flat
116	Beltsville, MD	12/31/88	39.03	76.82	46	Urban-Agric.	Flat
117	Laurel Hill State Park, PA	12/10/87	40.00	79.25	616	Forested	Complex
118	Big Meadows, VA	06/30/88	38.51	78.43	1,058	Forested	Mountaintop
119	Cedar Creek State Park, WV	11/09/87	38.83	80.90	274	Forested	Complex
120	Horton Station, VA	06/03/87	37.33	80.55	972	Forested	Mountaintop
121	Lilley Cornett Woods, KY	01/19/88	37.08	82.99	335	Forested	Complex
122	Oxford, OH	08/18/87	39.53	84.72	284	Agricultural	Rolling
123	Lykens, OH	09/30/88	40.92	83.00	296	Agricultural	Flat
124	Unionville, MI	06/30/88	43.61	83.42	198	Agricultural	Flat
126	Cranberry, NC	09/30/88	36.11	82.04	1,219	Forested	Mountaintop
127	Edgar Evins State Park, TN	03/22/88	36.04	85.73	302	Forested	Rolling
128	Arendtsville, PA	06/30/88	39.92	77.30	210	Agricultural	Rolling
129	Perryville, KY	08/11/87	37.68	84.97	279	Agricultural	Rolling
130	Bondville, IL	02/09/88	40.05	88.37	212	Agricultural	Flat

(continued)

TABLE 4. PRECISION AND ACCURACY OBJECTIVES FOR LABORATORY MEASUREMENTS FOR NDDN

Analyte	Sample Type	Method	Acceptance Criteria	
			Precision* (percent)	Accuracy+ (percent)
Ammonium (NH_4^+)	Filter Extract	Technicon AutoAnalyzer	10	90 to 110
Calcium (Ca^{+2})	Filter Extract	Inductively coupled plasma--atomic emission	10	90 to 110
Magnesium (Mg^{+2})	Filter Extract	Inductively coupled plasma--atomic emission	10	90 to 110
Sodium (Na^+)	Filter Extract	Inductively coupled plasma--atomic emission	10	90 to 110
Potassium (K^+)	Filter Extract	Inductively coupled plasma--atomic emission	10	90 to 110
Sulfate (SO_4^{-2})	Filter Extract	Ion chromatography	5	95 to 105
Nitrate (NO_3^-)	Filter Extract	Ion chromatography	5	95 to 105

*Determined from midlevel standard and initial calibration curve.
+Determined from reference traceable to the National Institute of Standards and Technology (NIST).

Source: Hunter/ESE, 1989.

character of sites. Midwestern sites are predominantly agricultural, while those in the northeast and southeast are mostly forested. Terrain characteristics also differ systematically between regions. The majority of midwestern sites are located on flat countryside and only that in eastern Kentucky (121--Lilley Cornett Woods) is in complex terrain. Northeastern sites in contrast are roughly evenly divided between rolling and complex terrain, and only one site (116--Beltsville, MD) is in flat terrain. Three northeastern sites are located above 1,000 meters (m) and form a line extending southward from northern Virginia to North Carolina. Site 118 (Big Meadows, VA) is situated at the crest of the Blue Ridge; Site 120 (Horton Station, VA) and Site 126 (Cranberry, NC) occupy the spine of the Appalachian Mountains. Due to the unique exposure of these sites, they have been placed in a separate terrain category (i.e., mountaintop).

Regional differences in terrain and land use, as reflected by the network, appear to faithfully represent actual differences between the midwest, northeast, and southeast. The midwest is indeed largely agricultural flatland, while the northeast is largely forested. By definition, the Appalachian Mountains and foothills are almost entirely contained within the northeastern and southeastern regions. Many of the sites classified as complex are located along the eastern and western flanks of the Appalachians. As will be discussed later, these regional differences in terrain and land use appear to exert significant influences over the air quality and meteorology observed across the network.

3.2 NETWORK OPERATIONS

This section summarizes the field, laboratory, and data management center (DMC) operations for the NDDN. Step-by-step protocols and additional details of these activities can be found in the NDDN Field Operations Manual, Laboratory Operations Manual, and Data Management Manual.

Ambient measurements for O_3, SO_2, SO_4^{-2}, NO_3^-, HNO_3, windspeed, wind direction, temperature, relative humidity, solar radiation, precipitation, and delta temperature were performed at each NDDN site. Meteorological parameters and O_3 concentrations were recorded continuously and reported as hourly averages. Atmospheric sampling for SO_4^{-2}, NO_3^-, HNO_3, and SO_2 was integrated over 7 day and night collection periods using a three-stage filter pack (see Figure 2). In this approach, particles and selected gases are collected by passing air at a controlled flow rate through a sequence of Teflon®, nylon, and base-impregnated filters. Filter packs were prepared and shipped to the field weekly and changed out at each site every Tuesday. Day filter pack samples were collected over the hours of 0800 to 2000 local standard time while night samples were collected over the remaining hours of the day. Blank filter packs were collected on a monthly basis to evaluate passive collection of particles and gases. At sites located more than 50 km from National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites, wet deposition monitoring equipment was installed. Precipitation samples will be collected weekly and shipped to the Hunter/ESE laboratory for chemical analyses beginning in 1989. Table 2 lists the equipment installed and operated at NDDN sites.

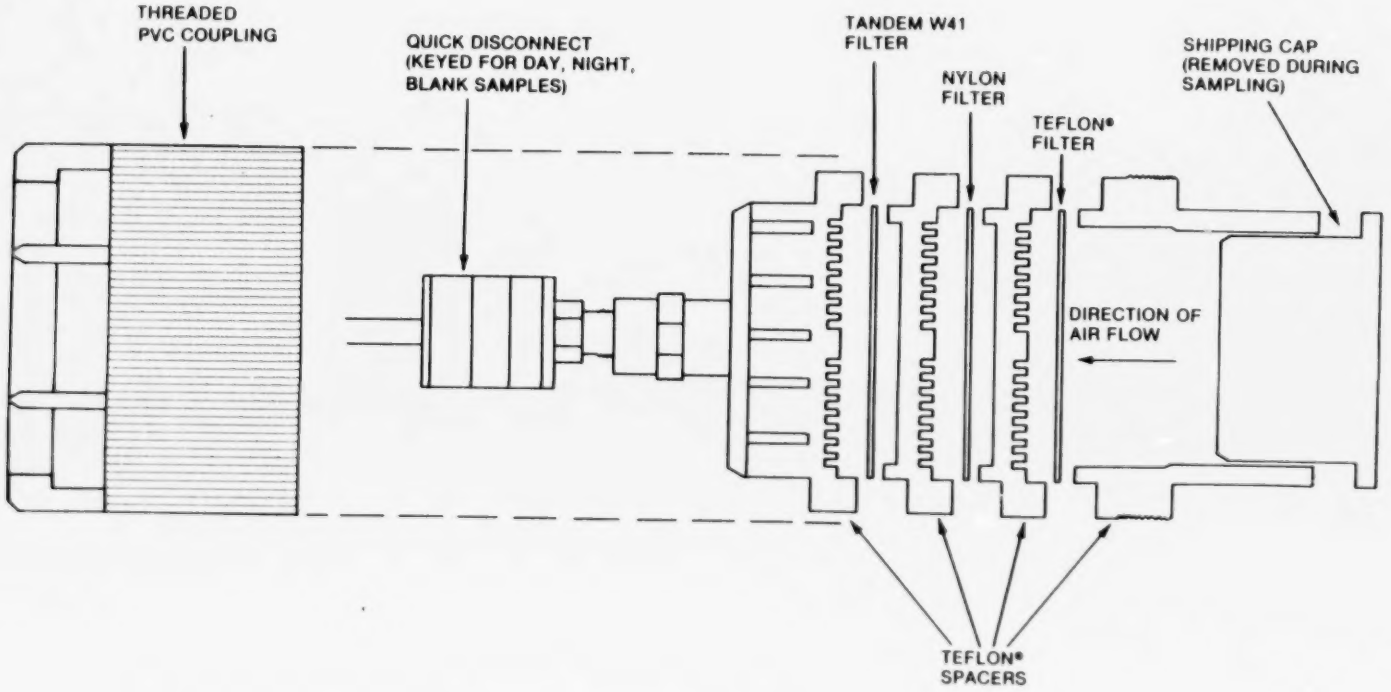

Figure 2. Filter pack assembly

TABLE 2. NDDN MONITORING EQUIPMENT

Item	Manufacturer	Model Number
Equipment Shelter [8 feet (ft) by 8 ft by 10 ft with electricity and telephone]	EKTO	8810
O_3 Analyzer	Thermo-Environmental	49-103
Meteorological System		
Windspeed	Climatronics	F460
Wind Direction	or	
Temperature	R.M. Young	AQ Series
Delta Temperature		
Relative Humidity		
Solar Radiation		
Precipitation (tipping bucket)		
10-Meter (m) Tower	Universal Mfg.	4-30
Data Acquisition System (DAS)		
Primary DAS	Odessa	SDM-3260
Backup DAS	Odessa	DSM-3260L
Personal Computer (PC)	Various	Various
Telecommunications Modem	Packard-Bell	2424
Printer	Star	SD-10
Air Quality Monitoring System		
10-Meter Tower	Aluma Tower	AT-048
Filter Packs	Savillex	--
Pump	Thomas	101-CA11
Flow Controller	Teledyne-Hastings	CST-10K
Solenoid Valve	Mace	800-2334
Wet Deposition Equipment (selected sites)		
Precipitation Collector	Andersen	APS
Rain Gauge (weighing)	Belfort	5915R-12
Triple-Beam Balance	Ohaus	1119-D

Source: Hunter/ESE, 1989.

3.2.1 Field Operations

Each site was equipped with a shelter (complete with telephone and 100-amp electrical service), two 10-m towers, a meteorological system, an O_3 and air quality monitoring system, and a data acquisition system (DAS). One tower was used for meteorological measurements, using a Climatronics F460 system or R.M. Young AQ system. Windspeed and wind direction were measured at 10 m, temperature was measured at 9 m and 2 m, and relative humidity was measured at 9 m. Precipitation and solar radiation were measured on 1-m platforms located outside the rain and sun shadows of the shelter and towers.

Filter pack sampling and O_3 measurements were performed at 10 m using a tilt-down aluminum tower (Aluma, Inc.). Day, night, and blank filter packs were fitted with non-interchangeable quick connects to prevent confusion and to reduce time for changeout in the field. Filter pack flow was maintained at 1.50 liters per minute (L/min) [for standard conditions of 25 degrees Celsius (°C) and 760 millimeters of mercury (mmHg)] with a Teledyne-Hastings CST-10K mass flow controller (MFC) and recorded as hourly averages on the data acquisition system. Switching from the day filter pack to the nighttime filter pack was performed by a relay-activated solenoid which was, in turn, controlled by the DAS.

O_3 was measured via ultra-violet absorbance with a Thermo-Environmental Model 49-103 analyzer operating on the 0 to 500 ppb range. Ambient air was drawn through an all-Teflon® sampling line upstream of the O_3 analyzer. A 3/8-inch TFE Teflon® sample line was used to sample air atop the 10-m air quality tower. Teflon® filters housed at the tower inlet and the analyzer inlet prevented particle deposition within the system. Periodic checks indicated that line losses through the inlet system were consistently less than 3 percent. Zero, precision (60 ppb), and span (400 ppb) checks of the O_3 analyzer were performed every third day using an internal O_3 generator.

The onsite DAS consisted of a primary datalogger (Odessa 3260), a back-up datalogger (Odessa 3260L), an IBM-compatible personal computer (PC), a printer, and a telephone modem. The primary datalogger was used to acquire, average, store, and communicate readings from all continuous sensors. It also performed a variety of control functions, such as switching the day/night filter pack relay and activating the internal O_3 generator for consistency checks. Data were stored on the primary and backup dataloggers in electronically erasable programmable read-only memory (EEPROM) cartridges, both of which were accessible through the onsite PC, or remotely, through the telephone modem. Printouts of hourly averages for the previous day were automatically generated by the onsite printer a few seconds after midnight each day.

Site operators visited each site on Tuesdays and Fridays and in response to equipment malfunctions or suspected problems. On Tuesdays, filter packs were changed out, sample lines were leak tested, sensors were

subjected to electronic and reasonableness checks, and data from the dataloggers were downloaded to diskettes. The site operator telephoned the NDDN operations center at Hunter/ESE following site inspections to relay observations and problems. Data, documentation, and samples were shipped to Hunter/ESE the day of collection. On Fridays, the site operator performed a similar but limited check of sensors and equipment.

All field equipment was subjected to inspections and multipoint calibrations (using standards traceable to the National Institute of Standards and Technology) by Hunter/ESE personnel on a quarterly basis. In addition, independent equipment audits were performed semiannually by ERC Environmental and Energy Services, Inc. (formerly Westec, Inc.) and randomly by EPA or its designee. Results of field calibrations were used to assess sensor accuracy and flag, adjust, or invalidate field data.

The overall precision of field measurements was evaluated by operation of dual sets of equipment at West Point, NY (i.e., Sites 103 and 104). Operation of Site 103 was terminated in October 1988 and, therefore, precision can be estimated only for the first three quarters of 1988. Plans were initiated for establishing five collocated sites in 1989 to provide precision information for the major geographical regions covered by the network. Precision and accuracy criteria for NDDN field measurements are shown in Table 3.

3.2.2 Laboratory Operations

Filter pack samples were loaded, shipped, received, extracted, and analyzed by Hunter/ESE personnel at the Gainesville, FL laboratory. The flow of samples through the laboratory is shown in Figure 3. Filter packs contained three types of filters in sequence: a Teflon® filter (Gelman, Zefluor, 1.0 μm) for collection of aerosols, a nylon filter (Gelman, 1.0 μm) for collection of HNO_3, and dual K_2CO_3 impregnated cellulose filters (Whatman 41) for collection of SO_2. All filters were subjected to acceptance tests before they were used in the network. Filters showing detectable levels of SO_4^{-2} or NO_3^- were either washed and re-tested or returned to the manufacturer for credit.

Following receipt from the field, exposed filters were placed in color-coded extraction bottles and extracted as shown in Figure 4. Extracts were then analyzed for SO_4^{-2} and NO_3^- by micromembrane suppressed ion chromatography (IC) using a Dionex Model 4000i IC equipped with an Autoion 1000 Controller. The instrumental configuration included a Dionex Automated Sampler, an AG4-A guard column, a AS4-A separator column, and a 50-microliter (μL) injection loop. Data acquisition, display, and analysis was accomplished with a Maxima computer integration system. The IC was calibrated prior to each analytical run with five standards plus a blank covering the range of 35 to 9,000 micrograms per liter (μg/L) for NO_3^- and 40 to 10,000 μg/L for SO_4^{-2}. Extraction and calibration solutions were spiked with 1.0 parts per million (ppm) particulate bromine (Br^-) as a check on IC column condition and to assist in detection of spurious sample injections.

TABLE 3. PRECISION AND ACCURACY OBJECTIVES OF FIELD MEASUREMENTS

Measurement Parameter	Method	Acceptance Criteria*	
		Precision	Accuracy
Windspeed (vector and scalar)	Anemometer	±0.5 m/sec	±0.2 m/sec
Wind direction	Wind vane	±5°	±2°
Standard deviation of wind direction	Wind vane	Undefined	Undefined
Relative humidity	Humidity sensor	±10% (of full scale)	±10%
Solar radiation	Pyranometer	±10% (of reading)	±10%
Precipitation	Rain gauge	±10% (of reading)	0.10 inch+
Ambient temperature	Thermistor	±0.5°C	±0.25°C
Delta temperature	Thermistor	±0.2°C	±0.1°C
Ozone (O_3)	O_3 analyzer	±10% (of reading)	±10%
Filter pack flow	Mass flow meter	±0.15 L/min	±10%

Note: ° = degree. L/min = liters per minute.
°C = degrees Celsius. m/sec = meters per second.

*Field precision criteria apply to collocated instruments; accuracy criteria apply to calibrations and audits of instruments.
+For target value of 1.00 inch.

Source: Hunter/ESE, 1989.

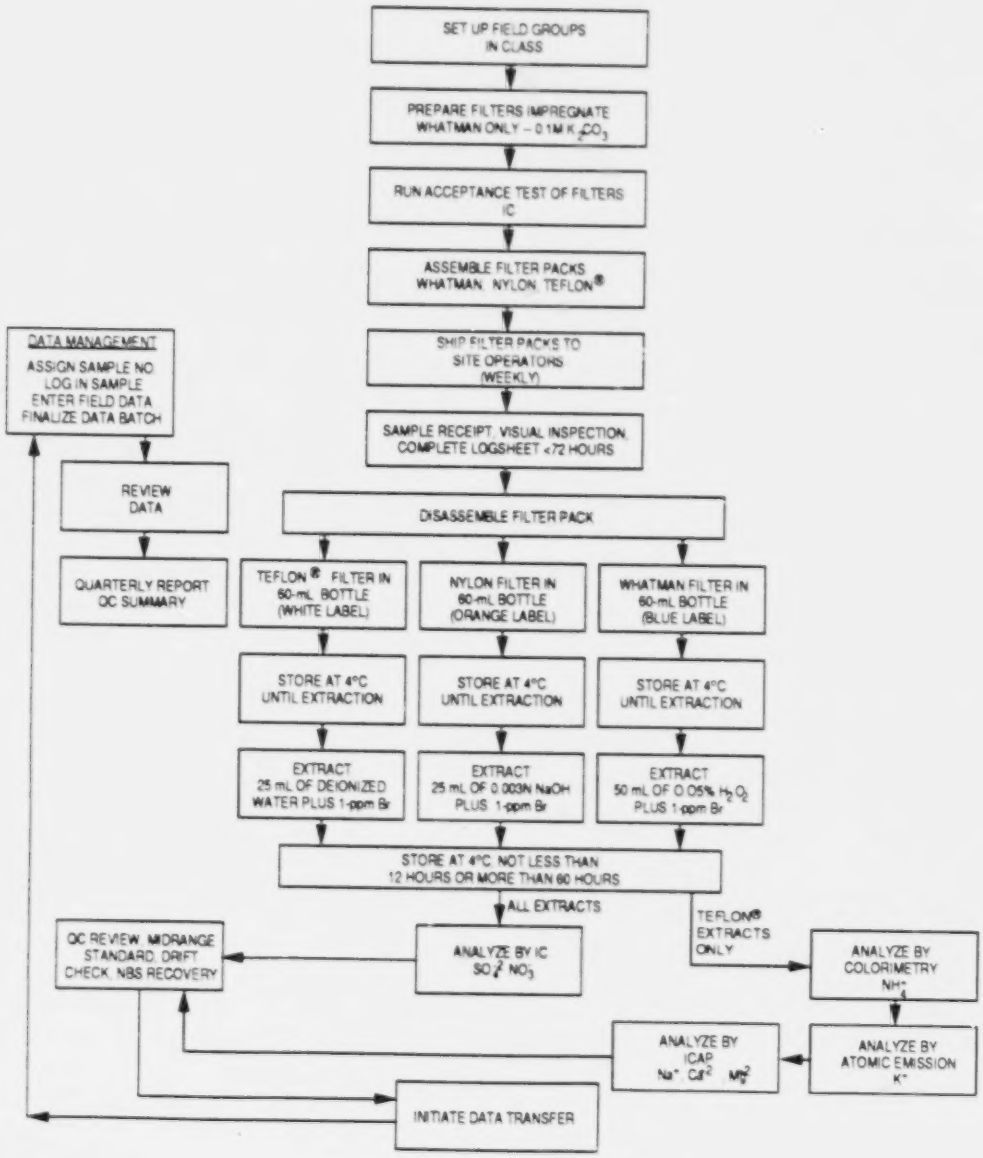
SET UP FIELD GROUPS IN CLASS
PREPARE FILTERS IMPREGNATE WHATMAN ONLY – 0.1M K_2CO_3
RUN ACCEPTANCE TEST OF FILTERS IC
ASSEMBLE FILTER PACKS WHATMAN, NYLON, TEFLON®
SHIP FILTER PACKS TO SITE OPERATORS (WEEKLY)
SAMPLE RECEIPT, VISUAL INSPECTION, COMPLETE LOGSHEET <72 HOURS
DISASSEMBLE FILTER PACK
DATA MANAGEMENT
ASSIGN SAMPLE NO.
LOG IN SAMPLE
ENTER FIELD DATA
FINALIZE DATA BATCH
REVIEW DATA
QUARTERLY REPORT QC SUMMARY
TEFLON® FILTER IN 60-mL BOTTLE (WHITE LABEL)
NYLON FILTER IN 60-mL BOTTLE (ORANGE LABEL)
WHATMAN FILTER IN 60-mL BOTTLE (BLUE LABEL)
STORE AT 4°C UNTIL EXTRACTION
STORE AT 4°C UNTIL EXTRACTION
STORE AT 4°C UNTIL EXTRACTION
EXTRACT 25 mL OF DEIONIZED WATER PLUS 1-ppm Br
EXTRACT 25 mL OF 0.003N NaOH PLUS 1-ppm Br
EXTRACT 50 mL OF 0.05% H_2O_2 PLUS 1-ppm Br
STORE AT 4°C NOT LESS THAN 12 HOURS OR MORE THAN 60 HOURS
ALL EXTRACTS
TEFLON® EXTRACTS ONLY
QC REVIEW, MIDRANGE STANDARD, DRIFT CHECK, NBS RECOVERY
ANALYZE BY IC SO_4^{-2} NO_3^-
ANALYZE BY COLORIMETRY NH_4^+
ANALYZE BY ICAP Na^+ Ca^{+2} Mg^{+2}
ANALYZE BY ATOMIC EMISSION K^+
INITIATE DATA TRANSFER

Figure 3. Flowchart of laboratory operations for filter pack samples

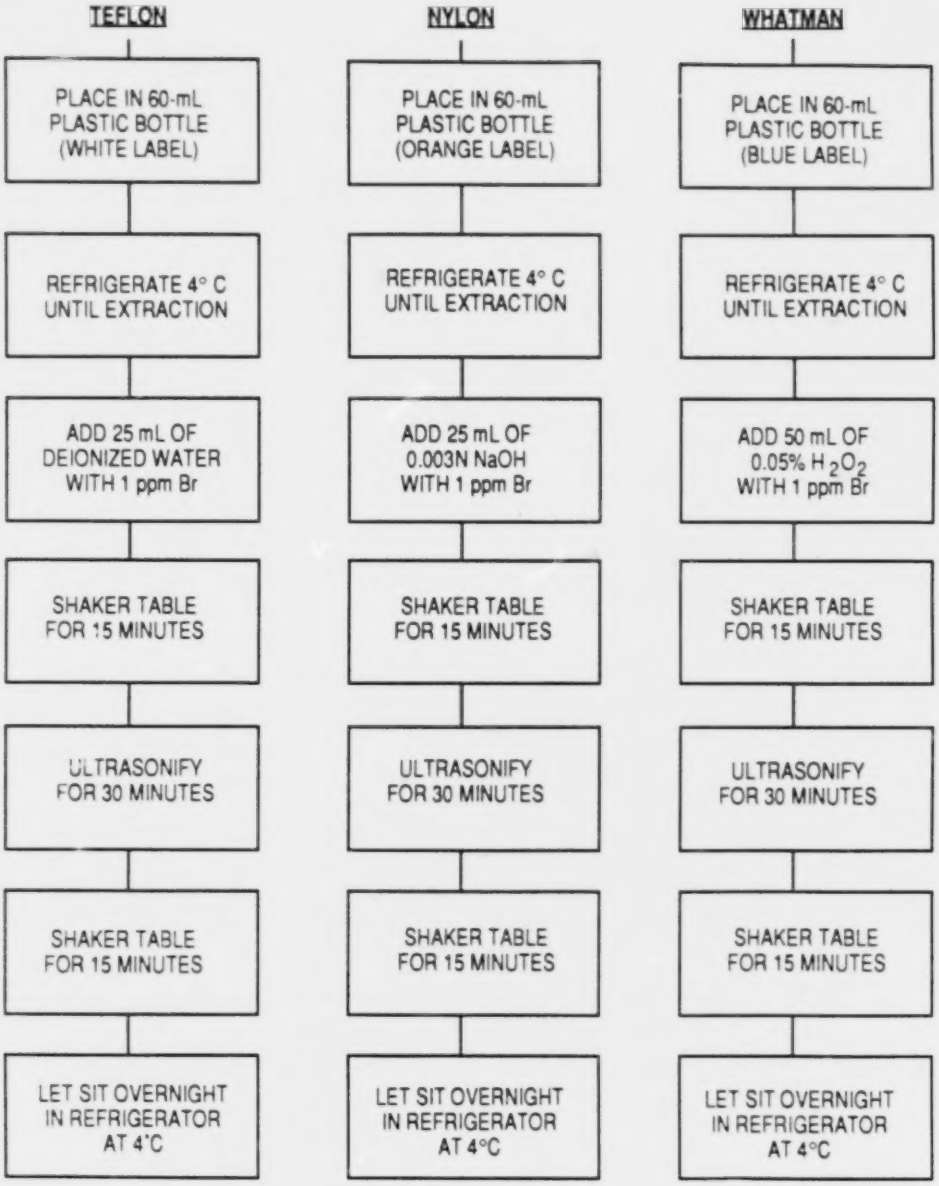
TEFLON
PLACE IN 60-mL PLASTIC BOTTLE (WHITE LABEL)
REFRIGERATE 4° C UNTIL EXTRACTION
ADD 25 mL OF DEIONIZED WATER WITH 1 ppm Br
SHAKER TABLE FOR 15 MINUTES
ULTRASONIFY FOR 30 MINUTES
SHAKER TABLE FOR 15 MINUTES
LET SIT OVERNIGHT IN REFRIGERATOR AT 4°C
NYLON
PLACE IN 60-mL PLASTIC BOTTLE (ORANGE LABEL)
REFRIGERATE 4° C UNTIL EXTRACTION
ADD 25 mL OF 0.003N NaOH WITH 1 ppm Br
SHAKER TABLE FOR 15 MINUTES
ULTRASONIFY FOR 30 MINUTES
SHAKER TABLE FOR 15 MINUTES
LET SIT OVERNIGHT IN REFRIGERATOR AT 4°C
WHATMAN
PLACE IN 60-mL PLASTIC BOTTLE (BLUE LABEL)
REFRIGERATE 4° C UNTIL EXTRACTION
ADD 50 mL OF 0.05% H_2O_2 WITH 1 ppm Br
SHAKER TABLE FOR 15 MINUTES
ULTRASONIFY FOR 30 MINUTES
SHAKER TABLE FOR 15 MINUTES
LET SIT OVERNIGHT IN REFRIGERATOR AT 4°C

Figure 4. Flowchart for extraction of NDDN air quality filters

Beginning in the third quarter of 1988, Teflon® filter extracts were analyzed routinely for NH_4^+, Na^+, K^+, Mg^{+2}, and Ca^{+2}. Analysis of Na^+, Mg^{+2}, and Ca^{+2} was performed with a Perkin-Elmer P-2 inductively coupled argon plasma (ICAP) emission spectrometer. Analysis of NH_4^+ was by the automated indophenol method using a Technicon II or TRAACS-800 AutoAnalyzer system. Analysis of K^+ was via atomic emission on a Perkin-Elmer 5100 atomic absorption spectrophotometer.

Various QC samples were routinely analyzed to track the accuracy and precision of laboratory data. NIST SRM No. 2694-II (simulated rainwater) was analyzed immediately after instrument calibration to monitor accuracy. Recoveries within ±5 percent of certified values were required for analyses to continue. A control sample was analyzed after every 10 environmental samples to monitor within-run precision. For the analytical batch to be accepted, the maximum difference between the first analysis and each subsequent analysis was limited to ±5 percent. Ten percent blind replicates were also analyzed to monitor between-run precision. Due to the potential for change in analyte concentration between analyses, replicate samples were not used as a control for acceptance of batches. Finally, one unknown sample provided by the EPA was analyzed with each batch. The unknown consisted of filter media spiked with salt solutions containing SO_4^{-2} and NO_3^-. These were carried through the entire extraction and analysis procedure established for Teflon®, nylon, and K_2CO_3-impregnated cellulose filters. Precision and accuracy objectives for NDDN laboratory analyses are listed in Table 4.

Results of all valid analyses were stored in units of micrograms per filter (μg/filter) in the laboratory data management system. Concentrations of all species were then calculated (based on volume of air sampled) following validation of hourly flow data. Atmospheric concentrations of particulate SO_4^{-2}, NO_3^-, NH_4^+, Na^+, K^+, Mg^{+2}, and Ca^{+2} were calculated based on the analysis of Teflon® filter extracts; HNO_3 was calculated based on the NO_3^- found in nylon filter extracts; and SO_2 was calculated based on the sum of SO_4^{-2} found in nylon and cellulose filter extracts. Since Teflon® filters were extracted in deionized water, it should be noted that reported concentrations of particulate species refer to the water soluble component only.

3.2.3 Data Management

Data management center activities consisted of three major operations: data acquisition, validation, and transmittal to EPA. These are depicted in Figure 5. The data acquisition process stressed multiple levels of redundancy in order to minimize data loss. The primary mode of data acquisition from the field was via telephone modem. Each site was automatically polled on a daily basis using a PC and software developed by Odessa Engineering, Inc. The polling software permits recovery of hourly data and status files, power failure logs, and automated calibration results from the previous 7 days. The program also maintains synchronization of the network by checking the clock within each DAS and correcting the time if it deviates from expectation by more than 2 minutes. If daily polling resulted in incomplete data capture from any site, then

TABLE 4. PRECISION AND ACCURACY OBJECTIVES FOR LABORATORY MEASUREMENTS FOR NDDN

Analyte	Sample Type	Method	Acceptance Criteria	
			Precision* (percent)	Accuracy+ (percent)
Ammonium (NH_4^+)	Filter Extract	Technicon AutoAnalyzer	10	90 to 110
Calcium (Ca^{+2})	Filter Extract	Inductively coupled plasma--atomic emission	10	90 to 110
Magnesium (Mg^{+2})	Filter Extract	Inductively coupled plasma--atomic emission	10	90 to 110
Sodium (Na^+)	Filter Extract	Inductively coupled plasma--atomic emission	10	90 to 110
Potassium (K^+)	Filter Extract	Inductively coupled plasma--atomic emission	10	90 to 110
Sulfate (SO_4^{-2})	Filter Extract	Ion chromatography	5	95 to 105
Nitrate (NO_3^-)	Filter Extract	Ion chromatography	5	95 to 105

*Determined from midlevel standard and initial calibration curve.
+Determined from reference traceable to the National Institute of Standards and Technology (NIST).

Source: Hunter/ESE, 1989.

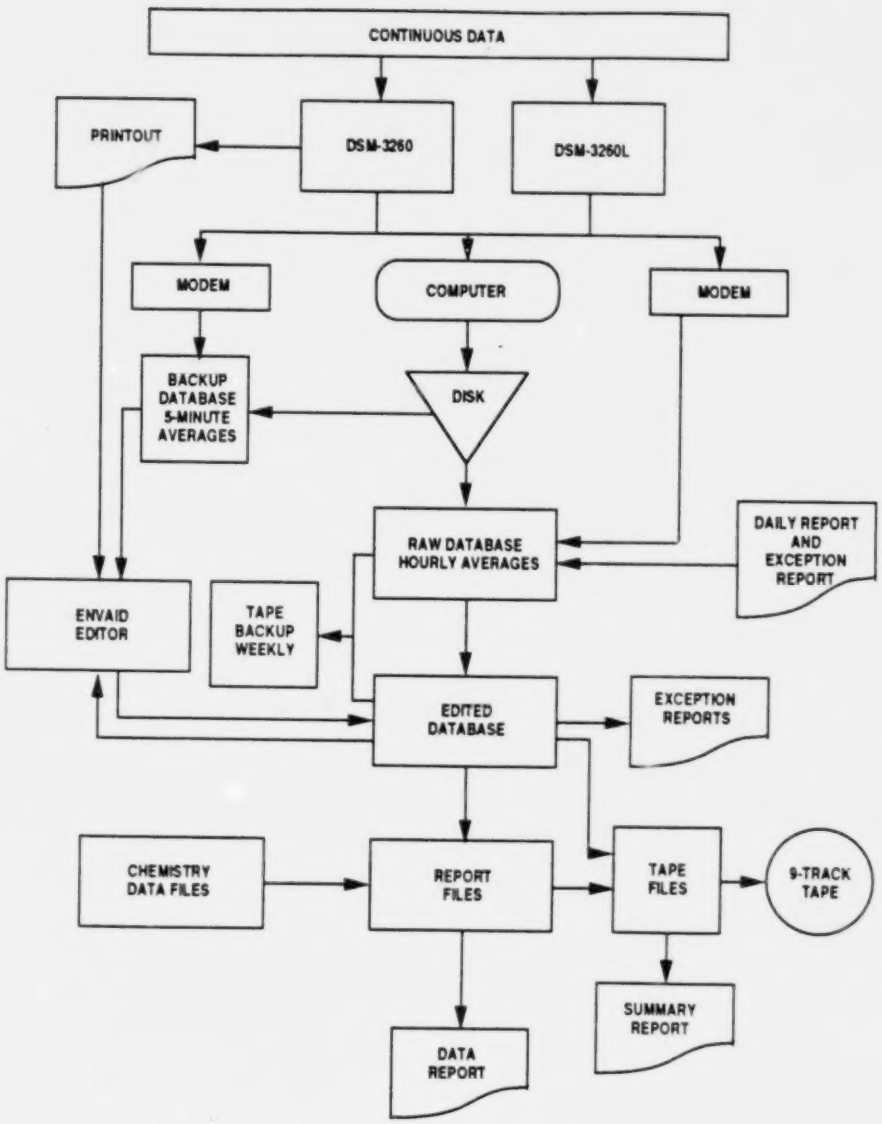

Figure 5. Flow of data through the NDDN data management system

diskettes of data from the primary and backup DAS were read into the database management system. If the database was still incomplete, then missing data were entered manually from site printouts. Each datum was automatically given a source flag that could be used to trace its mode of entry into the system (i.e., modem, primary DAS, backup DAS, or printout).

Data validation consisted of thorough review of operator logs, onsite reasonableness checks, results of field calibrations and audits and a variety of parameter-specific range and consistency checks. In addition, diurnal patterns for numerous parameters and a variety of inter-parameter relationships were examined for reasonableness. Solar radiation data, for example, were used to check for time shift errors in the database (caused by power failure), while significant rainfall events were used to check the response of relative humidity and temperature sensors (the former should approach 100 percent, and delta temperature should approach zero).

Following validation of data for a calendar quarter, flag counts, and parameter averages were calculated. The database, flag counts, and averages were then loaded onto a 9-track tape and submitted to the NDDN Project Officer. To verify the data transfer, flag counts and parameter averages were independently generated by EPA and echoed back to Hunter/ESE. Data sets were subjected to a variety of reasonableness and consistency checks by EPA before final acceptance into the NDDN database.

SECTION 4.0

RESULTS AND DISCUSSION

4.1 FILTER PACK MEASUREMENTS

4.1.1 Annual Concentration Data

Annual arithmetic average concentrations of SO_4^{-2}, NO_3^-, HNO_3, and SO_2 are shown in Figures 6 and 7 for 18 sites in operation throughout 1988. Aerosol SO_4^{-2} concentrations range from 7.5 $\mu g/m^3$ in northern West Virginia (Site 107) to 3.4 $\mu g/m^3$ in northern New York (Site 105). Concentrations above 7.0 $\mu g/m^3$ occur in a band extending from southwestern Pennsylvania to Virginia and also in central Kentucky. Concentrations of 5.0 to 5.9 $\mu g/m^3$ extend around virtually the entire periphery of the network from northern Illinois to southwestern North Carolina to northern New York. A strong concentration gradient (i.e., factor of 2) occurs between the local maximum in West Virginia and northern New York. Weaker gradients extend southeastward and northwestward from the locus of concentrations above 7.0 $\mu g/m^3$.

Aerosol NO_3^- concentrations exhibit much more variability than SO_4^{-2} and a definite pattern of higher concentrations in the midwest than elsewhere. The lowest concentrations (<0.3 $\mu g/m^3$) are observed in forested sites in the Adirondack and Appalachian Mountains (i.e., Site 105 and Site 137), while the highest concentrations (>2.0 $\mu g/m^3$) are observed in urban and agricultural areas of the midwest. The only northeastern site to exhibit annual NO_3^- concentrations in excess of 1.0 $\mu g/m^3$ was located on a research farm operated by the Pennsylvania State University (Site 106). This observation supports the notion of a linkage between agricultural activity and NO_3^- concentrations. Two potential mechanisms for NO_3^- production include gas phase reaction of HNO_3 and NH_3 and gas-particle reaction of HNO_3 with soil particles. Both of these reactions are likely to be enhanced in agricultural areas, relative to forested areas.

Annual averages for HNO_3 exhibit maximum concentrations around 3.5 $\mu g/m^3$ in central Kentucky and southwestern Virginia and minimum concentrations of 1.1 $\mu g/m^3$ in eastern Kentucky and southwestern North Carolina. The majority of concentrations networkwide fall in the range of 2.5 to 3.0 $\mu g/m^3$. The overall pattern for HNO_3 might be influenced by terrain as much or more than other factors (e.g., emissions). Sites with the highest average values typically have good exposure to wind flow (fetch) while those with the lowest values typically have poor exposure due mainly to complex terrain. For a species, such as HNO_3, with a relatively

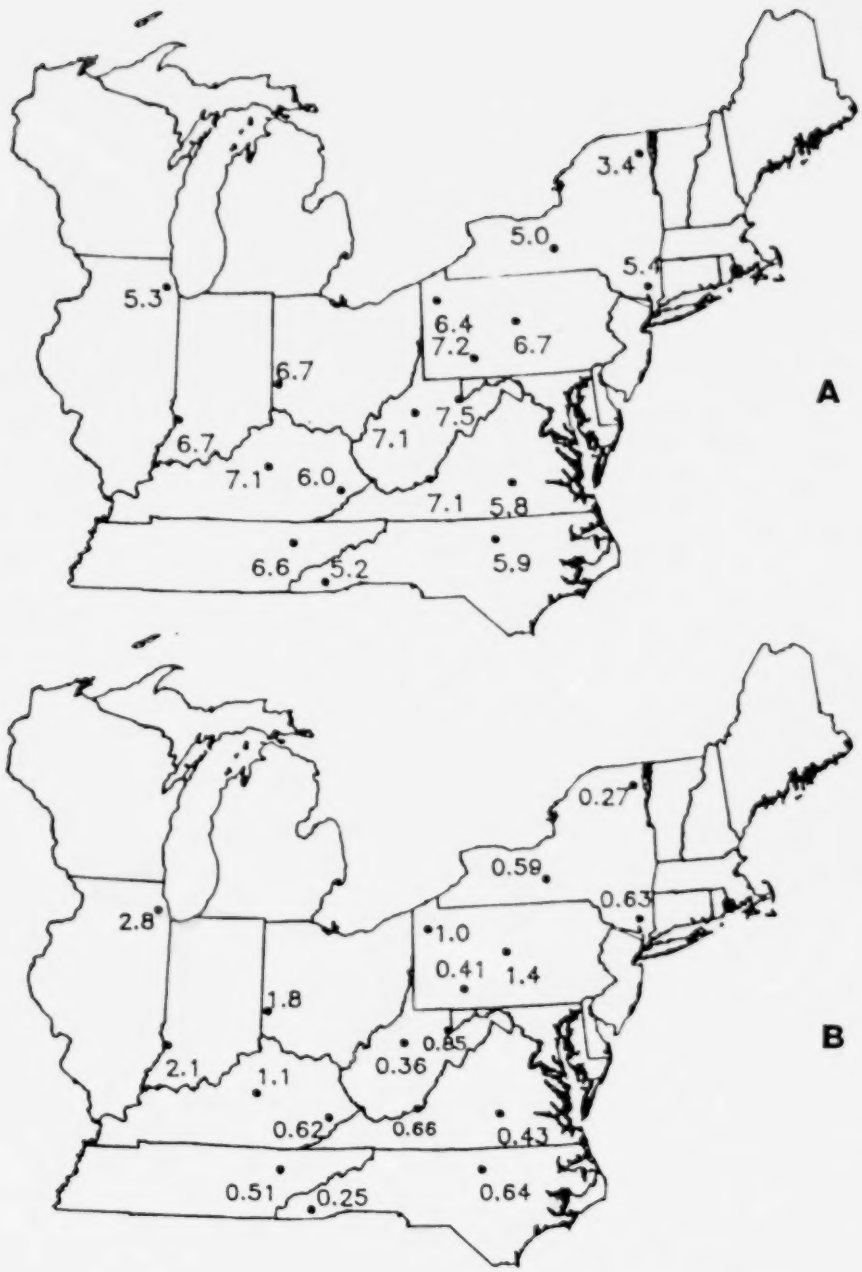

Figure 6. Annual average concentration of SO_4^{-2} (A) and NO_3^- (B) ($\mu g/m^3$) for 1988

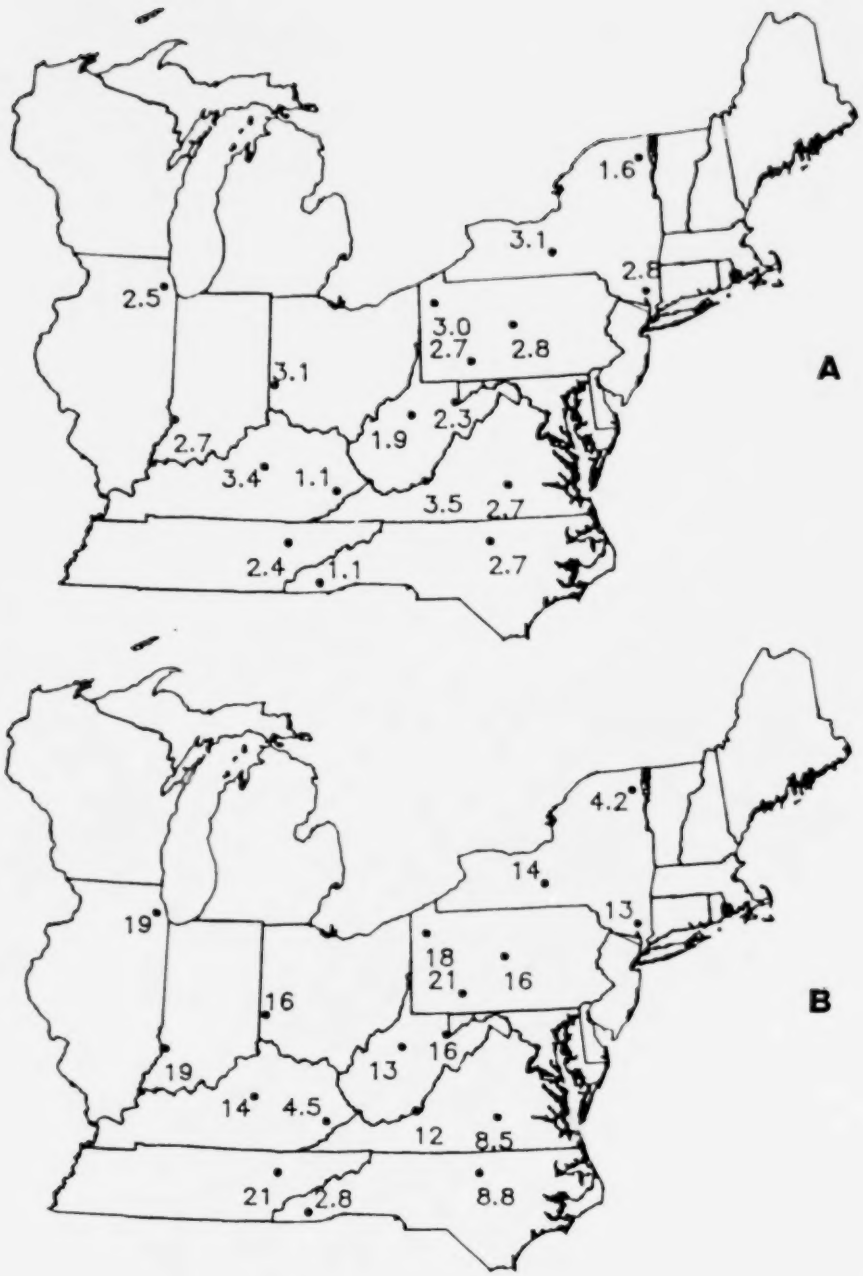

Figure 7. Annual average concentration of HNO_3 (A) and SO_2 (B) ($\mu g/m^3$) for 1988

high deposition velocity, the microclimate in regions of complex terrain could induce small-scale variability in atmospheric concentrations.

Results for SO_2 show maximum annual concentrations around 20 $\mu g/m^3$ in western Pennsylvania, eastern Tennessee, and northern Illinois, and minimum concentrations below 5.0 $\mu g/m^3$ in southwestern North Carolina, northern New York, and eastern Kentucky. Large concentration gradients (i.e., factor of 3 or more) occur within the states of New York and Kentucky and across the southern Appalachians from Tennessee to North Carolina. Other than the relatively high values in eastern Tennessee, the overall pattern is reminiscent of that for HNO_3.

Average concentrations for 1987 and 1988 are compared for five sites in Table 5. Results show highly consistent concentrations from year to year. SO_4^{-2} values differ by up to 1.0 $\mu g/m^3$, or approximately 14 percent at Site 102, but are not significantly different for any site at the 95-percent confidence level. Annual averages for NO_3^- differ by no more than 0.1 $\mu g/m^3$, which is on the order of magnitude of the field precision of the sampling/analysis protocol currently in use (see Section 4.5). Similar results are obtained for HNO_3 and SO_2. In general, the data presented in Table 5 indicate no evidence of significant inter-annual variability (based on two years of data).

4.1.2 Seasonal Concentration Data

4.1.2.1 First Quarter 1988

Average concentrations of SO_4^{-2}, NO_3^-, HNO_3, and SO_2 for first quarter of 1988 are shown in Figures 8 and 9. Results show unique patterns for each species, but in all cases the lowest values are observed at the northern and southern extremes of the Appalachian Mountains (i.e., Site 105 and Site 137). For SO_4^{-2}, quarterly averages range from 2.5 $\mu g/m^3$ at Site 105 to 4.9 $\mu g/m^3$ at Site 106 and are slightly higher in the eastern and southeastern sites than the midwestern sites. Two strong concentration gradients occur between central Pennsylvania and upstate New York and between eastern Tennessee and southwestern North Carolina.

Aerosol NO_3^- concentrations range from 0.3 $\mu g/m^3$ (Sites 105 and 137) to 4.1 $\mu g/m^3$ (Site 146) and show characteristic differences between the midwest (i.e., Ohio, Indiana, and Illinois) and the northeast. Midwestern concentrations of NO_3^- are uniformly above 2.0 $\mu g/m^3$ (mean 3.1 $\mu g/m^3$), while all other sites except central Pennsylvania are below 2.0 $\mu g/m^3$ (mean 0.8 $\mu g/m^3$). This pattern may be related to higher levels of dust and/or ammonia in the agricultural midwest than in the forested northeast.

HNO_3 data for the quarter range from 1.2 $\mu g/m^3$ at Site 146 to 3.5 $\mu g/m^3$ at Site 120. The lowest values (i.e., below 2.0 $\mu g/m^3$) are observed in northern New York, western North Carolina, and Illinois and highest values (i.e., above 3.0 $\mu g/m^3$) in central New York, Kentucky, and southwestern Virginia. Due to its high deposition velocity, the spatial distribution of HNO_3 is likely more sensitive to elevation and exposure of sites than any of the other measured parameters. This might explain what

TABLE 5. COMPARISON OF ANNUAL AVERAGE CONCENTRATIONS AT FIVE SITES FOR 1987 AND 1988*

	Site	Year	SO_4^{-2}	NO_3^-	HNO_3	SO_2
101	Research Triangle Park, NC	1987	6.0 ±3.4	0.63 ±0.38	2.6 ±1.1	8.1 ±5.6
		1988	5.9 ±3.7	0.64 ±0.37	2.7 ±1.2	8.8 ±4.9
102	Oak Ridge, TN	1987	7.6 ±6.1	0.58 ±0.36	2.7 ±0.83	20 ±9.7
		1988	6.6 ±5.4	0.51 ±0.34	2.4 ±0.88	21 ±9.4
104	West Point, NY	1987	5.4 ±2.8	0.62 ±0.27	2.7 ±0.96	12 ±6.7
		1988	5.4 ±3.0	0.63 ±0.28	2.8 ±0.87	13 ±6.6
105	Whiteface Mountain, NY	1987	3.0 ±1.7	0.29 ±0.15	1.5 ±0.75	3.7 ±1.6
		1988	3.4 ±1.9	0.27 ±0.13	1.6 ±0.84	4.2 ±1.8
106	Penn State University, PA	1987	7.2 ±3.2	1.5 ±0.62	3.0 ±1.4	17 ±8.8
		1988	6.7 ±3.3	1.4 ±0.59	2.8 ±1.2	16 ±8.7

*Values shown indicate arithmetic average and standard deviation.

Source: Hunter/ESE, 1989.

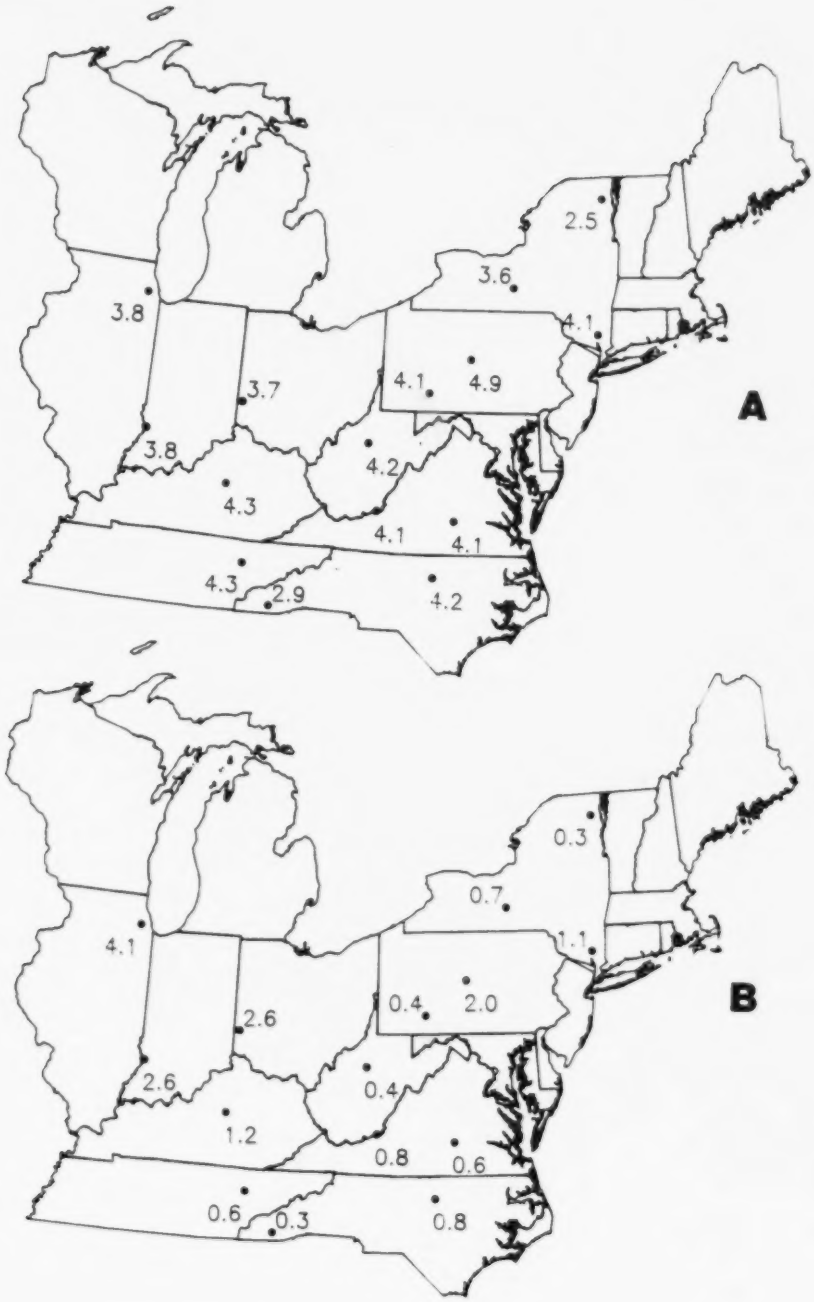

Figure 8. Average SO_4^{-2} (A) and NO_3^- (B) concentrations ($\mu g/m^3$)--first quarter 1988

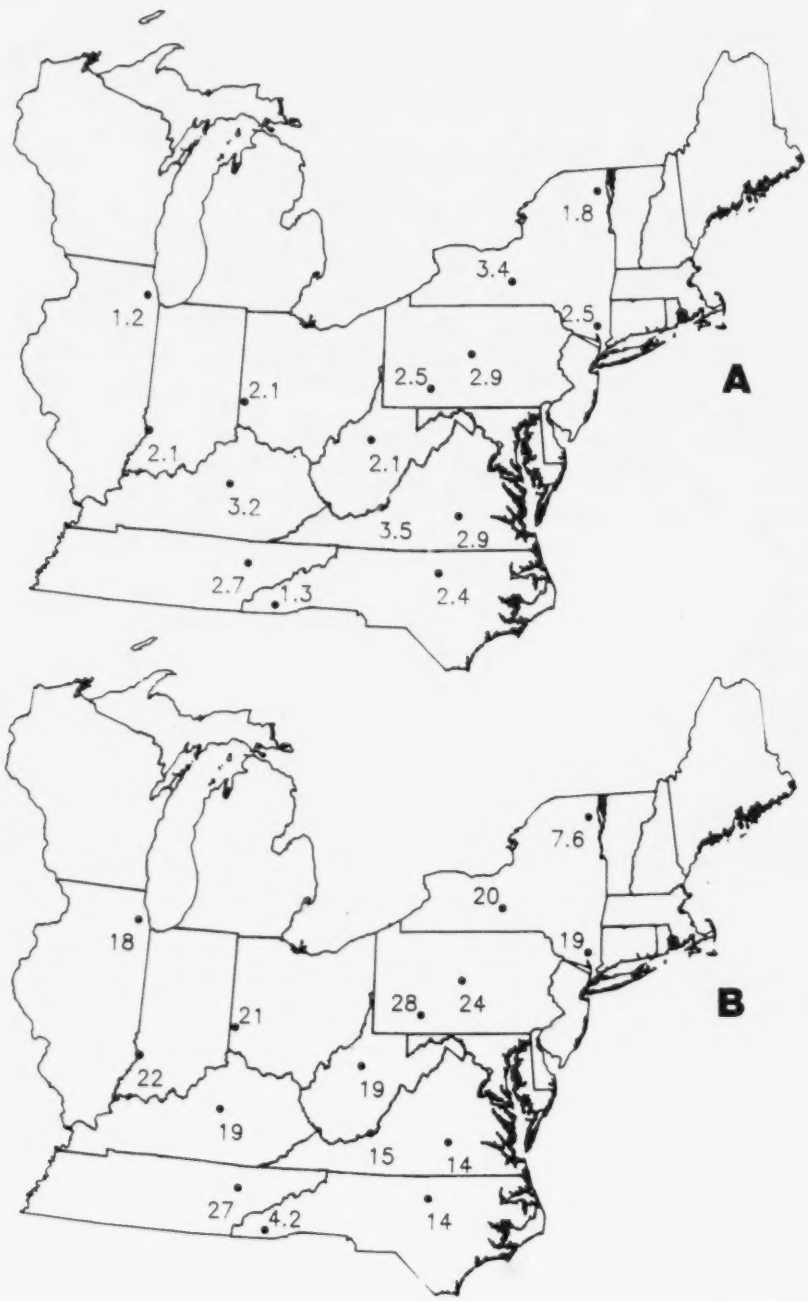

Figure 9. Average HNO_3 (A) and SO_2 (B) concentrations ($\mu g/m^3$)--first quarter 1988

appear to be somewhat depressed concentrations at sites located in the complex terrain of central West Virginia and southwestern North Carolina. Relatively low HNO_3 in the midwest versus the northeast could be related to gas scavenging by alkaline dust particles or to reactions with atmospheric NH_3, both of which might be present at higher concentrations in agricultural areas than in forested areas.

The SO_2 pattern for the period shows considerable spatial variability. Quarterly average values range from 4.2 $\mu g/m^3$ in southwestern North Carolina to 28 $\mu g/m^3$ in southwestern Pennsylvania. A pronounced gradient occurs across New York state and a moderate gradient occurs from the midwest to Virginia and North Carolina. Results for eastern Tennessee (Site 102-Oak Ridge, TN) are significantly higher than those for western North Carolina and central Kentucky, suggesting local influences. Indeed, Site 102 is ringed by a large number of SO_2 point sources. Data from Site 127 in central Tennessee should assist in evaluating the magnitude of local influences in the Oak Ridge area.

4.1.2.2 Second Quarter 1988

Average concentration data for SO_4^{-2}, NO_3^-, HNO_3, and SO_2 for second quarter 1988 are shown in Figures 10 and 11. As was observed for the first quarter, lowest overall concentrations are typically found in upstate New York (Site 105) and southwestern North Carolina (Site 137). SO_4^{-2} values range from 9.3 $\mu g/m^3$ at Horton Station, VA (Site 120), to 3.0 $\mu g/m^3$ at Whiteface Mountain, NY (Site 105). The highest SO_4^{-2} concentrations for the quarter (i.e., >8.0 $\mu g/m^3$) were found in a band of sites from eastern Tennessee to southwestern Pennsylvania. From this band, concentrations drop off gradually to the east and northwest but dramatically to the northeast (i.e., through Pennsylvania and New York state). As expected, the overall SO_4^{-2} pattern is relatively smooth and suggests a slight easterly displacement of peak concentrations with respect to the major source areas of SO_2.

Aerosol NO_3^- concentrations range from 0.24 $\mu g/m^3$ (Site 137) to 2.0 $\mu g/m^3$ (Site 146) and show characteristic differences between the midwest and northeast. Midwestern concentrations are generally at or above 1.0 $\mu g/m^3$, whereas northeastern concentrations are usually well below 1.0 $\mu g/m^3$. As mentioned previously, this pattern appears to reflect differences in land use between the two regions. The midwestern sites are typically located in or near areas of heavy agriculture, whereas the northeastern sites are typically located in rural-forested settings. The principal exception to this is Site 106, which occupies an agricultural research farm of the Pennsylvania State University, and, perhaps coincidentally, is the only site in the northeast with NO_3^- concentrations above 1.0 $\mu g/m^3$. Thus, agricultural activity appears to correlate with aerosol NO_3^- concentrations.

Quarterly average HNO_3 concentrations range from 1.5 $\mu g/m^3$ (Site 105 and 137) to 4.2 $\mu g/m^3$ (Sites 122 and 129) and exhibit a tendency for slightly higher concentrations in the midwest than elsewhere. As expected for a secondary air pollutant, the overall pattern is relatively free of

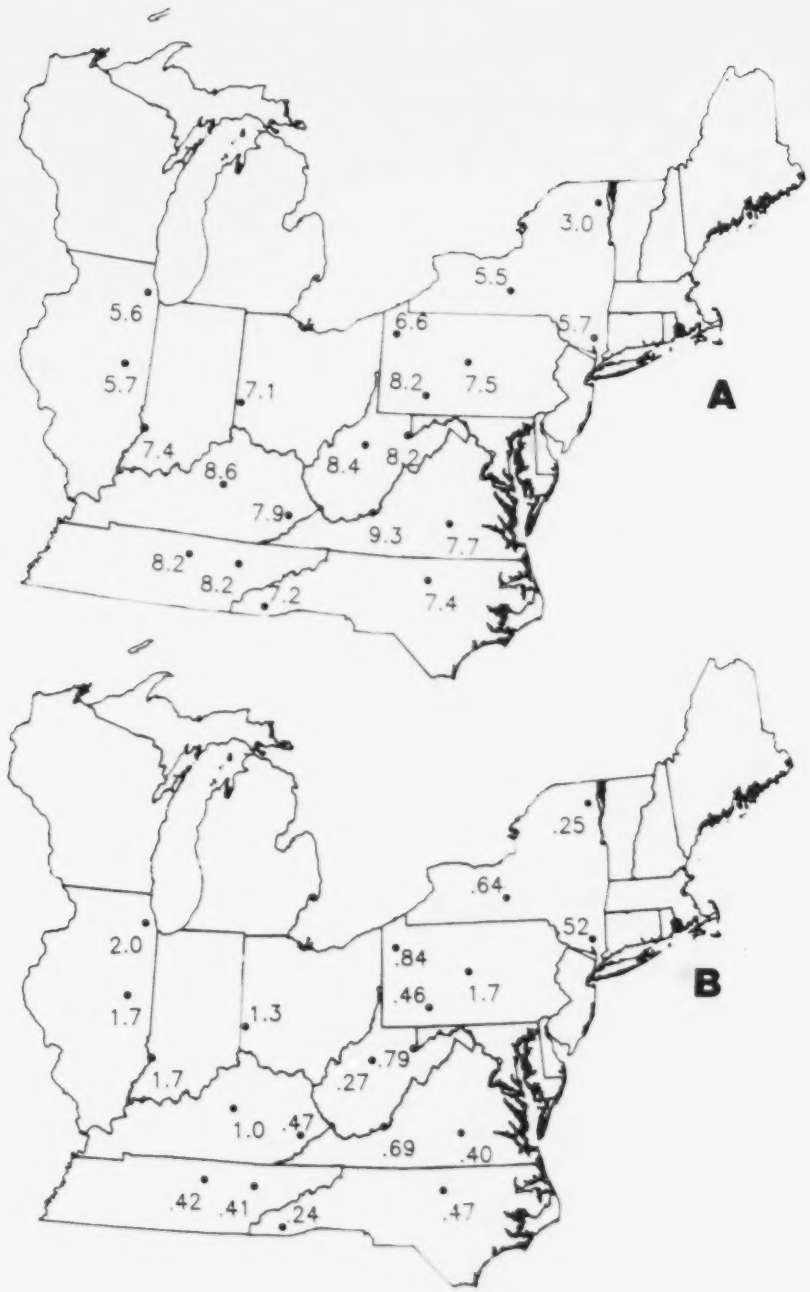

Figure 10. Average SO_4^{-2} (A) and NO_3^- (B) concentrations ($\mu g/m^3$)--second quarter 1988

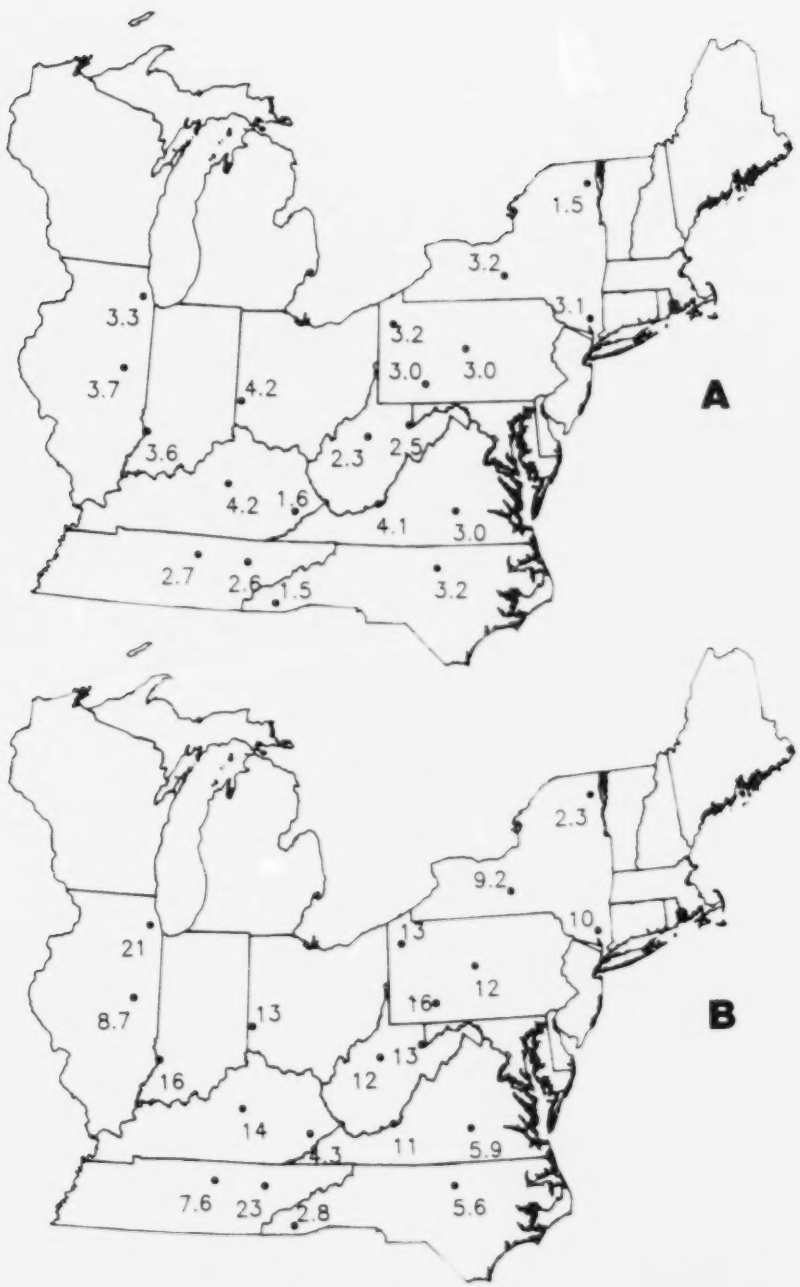

Figure 11. Average HNO_3 (A) and SO_2 (B) concentrations ($\mu g/m^3$)--second quarter 1988

sharp concentration gradients. Average concentrations for West Virginia and eastern Kentucky, however, are slightly to markedly lower than for surrounding sites. This suggests that HNO_3, with its high deposition velocity, may be strongly influenced by microclimate and/or terrain. In areas of extremely complex terrain (such as eastern Kentucky and West Virginia), it is conceivable that valleys and ridges are both representative and that differences in microclimate will cause sharp gradients in the ambient concentration of rapidly depositing species.

SO_2 concentrations range from 2.3 $\mu g/m^3$ (Site 105) to 23 $\mu g/m^3$ (Site 102) and are generally above 10 $\mu g/m^3$ from Indiana eastward through Ohio, Kentucky, and Pennsylvania and below 10 $\mu g/m^3$ elsewhere. Persistently high concentrations in eastern Tennessee and northern Illinois (Sites 102 and 146) are almost certainly the result of local emissions. Results for the eastern Kentucky site (121) and the southwestern North Carolina site (137) show marked concentration depressions, indicating that SO_2, like HNO_3, may be sensitive to microclimate.

4.1.2.3 Third Quarter 1988

Average concentration data for SO_4^{-2}, NO_3^-, HNO_3, and SO_2 during the third quarter 1988 are depicted in Figures 12 and 13. Average SO_4^{-2} values range from 13.3 $\mu g/m^3$ at Parsons, WV (Site 107) to 4.7 $\mu g/m^3$ at Wellston, MI (Site 149). The highest SO_4^{-2} concentrations (i.e., >10 $\mu g/m^3$) for the quarter were found in a band of sites extending from southwestern Indiana to central Pennsylvania and the mountains of Virginia. From this band, concentrations drop off gradually to the east and northwest and rapidly to the northeast (i.e., through Pennsylvania and New York state). Relatively strong gradients in concentration occur in Michigan and New York state. In both cases, concentrations decrease by 30 to 40 percent from south to north over a distance of a few hundred kilometers.

Aerosol NO_3^- concentrations range from less than 0.2 $\mu g/m^3$ (Sites 137, 102, and 119) to 2.0 $\mu g/m^3$ (Site 146) and show characteristic differences between the midwest and northeast. Midwestern concentrations, except for Site 149, are above 0.75 $\mu g/m^3$, while northeastern concentrations, except for Site 128, are invariably below 0.75 $\mu g/m^3$.

Quarterly average HNO_3 concentrations range from 0.9 $\mu g/m^3$ (Site 137) to 4.7 $\mu g/m^3$ (Site 128). Concentrations above 3.0 $\mu g/m^3$ occur in all states except Tennessee, Georgia, and West Virginia. As for SO_4^{-2}, concentration gradients are found in Michigan and New York state. Unlike SO_4^{-2}, sharp gradients also are found in areas of complex terrain extending from southwestern North Carolina to northern West Virginia. Sites 137, 121, 120, and 107 show slightly to markedly depressed concentrations with respect to neighboring sites.

SO_2 concentrations range from 1.1 $\mu g/m^3$ (Site 137) to 19.8 $\mu g/m^3$ (Site 146) and are generally above 10 $\mu g/m^3$ from southern Illinois eastward through Ohio and Pennsylvania. Concentrations around the periphery of the network (i.e., northern New York, northern Michigan, and central Georgia) are on the order of 2 to 4 $\mu g/m^3$. Relatively high concentrations in

Figure 12. Average SO_4^{-2} (A) and NO_3^- (B) concentrations ($\mu g/m^3$)--third quarter 1988

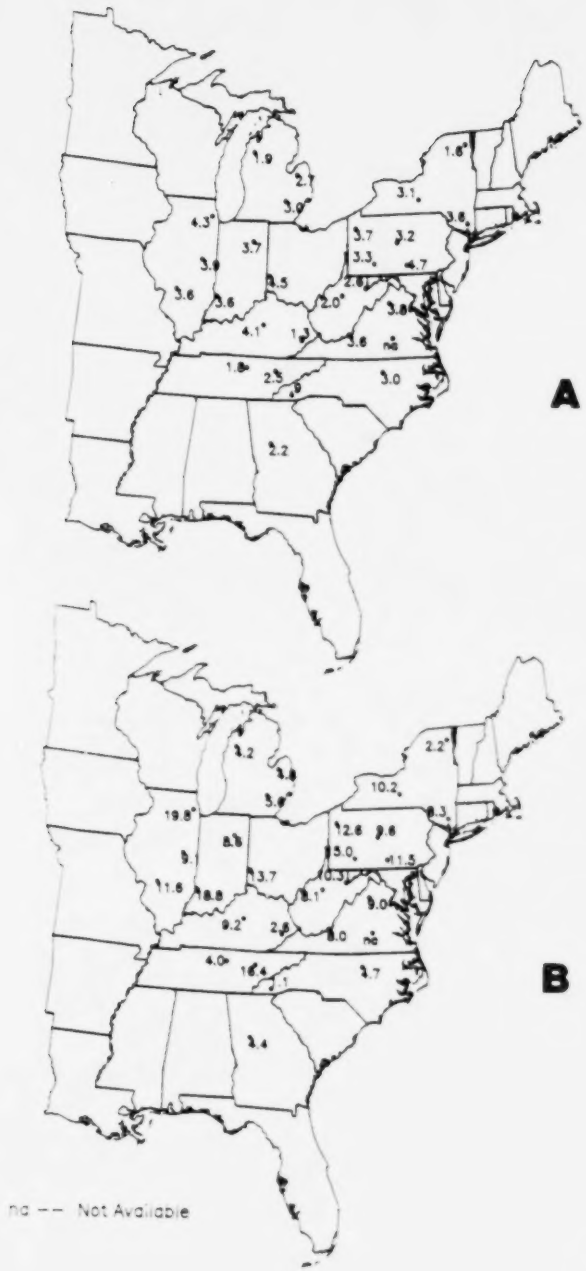

Figure 13. Average HNO_3 (A) and SO_2 (B) concentrations ($\mu g/m^3$)-- third quarter 1988

eastern Tennessee, northern Illinois, and southwestern Indiana (Sites 102, 140, and 146) appear to reflect local emissions. Relatively low concentrations for sites in eastern Kentucky and southwestern North Carolina (121 and 137) suggest that SO_2 exposure may be strongly influenced by terrain, as well as remoteness from sources.

4.1.2.4 Fourth Quarter 1988

Average concentrations for SO_4^{-2}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{+2}, Mg^{+2}, HNO_3, and SO_2 for the fourth quarter 1988 are depicted in Figures 14 through 18. Average SO_4^{-2} concentrations for the quarter range from 2.3 $\mu g/m^3$ at Site 105 (Whiteface Mountain, NY) to 4.0 $\mu g/m^3$ at Sites 101 and 102 (Research Triangle Park, NC; and Oak Ridge, TN), and show remarkably constant values from the Mississippi River to the Atlantic seaboard. Significant gradients occur in latitudinal transects through the states of New York and Michigan where values decrease by about 30 percent from north to south. Relatively low concentrations at Sites 121 and 137 (both averaged 2.9 $\mu g/m^3$ during the quarter) and, to a lesser extent, Site 119 (3.2 $\mu g/m^3$), could be terrain related. Results for Site 150 (Caddo Valley, AR), the most westerly site in operation for the entire quarter could reflect the transition from expectedly low concentrations in the great plains and far west to high concentrations in the east.

NO_3^- concentrations varied by more than an order of magnitude across the network and ranged from 0.26 $\mu g/m^3$ at Site 137 (Coweeta, NC) to 3.4 $\mu g/m^3$ at Site 133 (Salamonie Reservoir, IN). In general, concentrations are above 2.0 $\mu g/m^3$ in the midwestern states of Illinois, Wisconsin, Indiana, Ohio, and Michigan (except for the extreme northern site) and well below 1.0 $\mu g/m^3$ nearly everywhere else. The states of Kentucky and Pennsylvania exhibited intermediate concentrations in the range of 1.0 to 2.0 $\mu g/m^3$, perhaps reflecting transport of aerosol NO_3^- from the midwest.

Quarterly NH_4^+ concentrations ranged from 0.66 $\mu g/m^3$ at Site 105 to 2.1 $\mu g/m^3$ at Site 133 and were slightly higher in the midwest than elsewhere. The overall pattern of NH_4^+ concentrations was similar to that for SO_4^{-2}, perhaps reflecting a chemical association between the two (i.e., ammonium sulfates). For most sites in the northeast, there is sufficient NH_4^+ (on an equivalent basis) to completely account for ambient SO_4^{-2} concentrations. In the midwest, there is excess NH_4^+ with respect to SO_4^{-2}, which suggests that some ammonium nitrate (NH_4NO_3) could be present in the atmosphere.

Results for Na^+ range from 54 nanograms per cubic meter nanograms per cubic meter (ng/m^3) at Site 105 to 250 ng/m^3 at Site 101 and suggest marine influences along the Atlantic coast from New York to Georgia. Although no site is within 50 km of the coast, the four closest sites (Sites 101, 104, 108, and 153) average 188 ng/m^3, whereas the remaining sites average (87 ng/m^3). Relatively high Na^+ concentrations at Site 146 (160 ng/m^3) almost certainly reflect urban influences of the Chicago metropolitan area (e.g., road salt). Na^+ is frequently used to determine marine-derived SO_4^{-2} in precipitation and aerosols, based on the ratio of Na^+ to SO_4^{-2} in bulk

Figure 14. Average SO_4^{-2} (A) and NO_3^- (B) concentrations ($\mu g/m^3$)--fourth quarter 1988

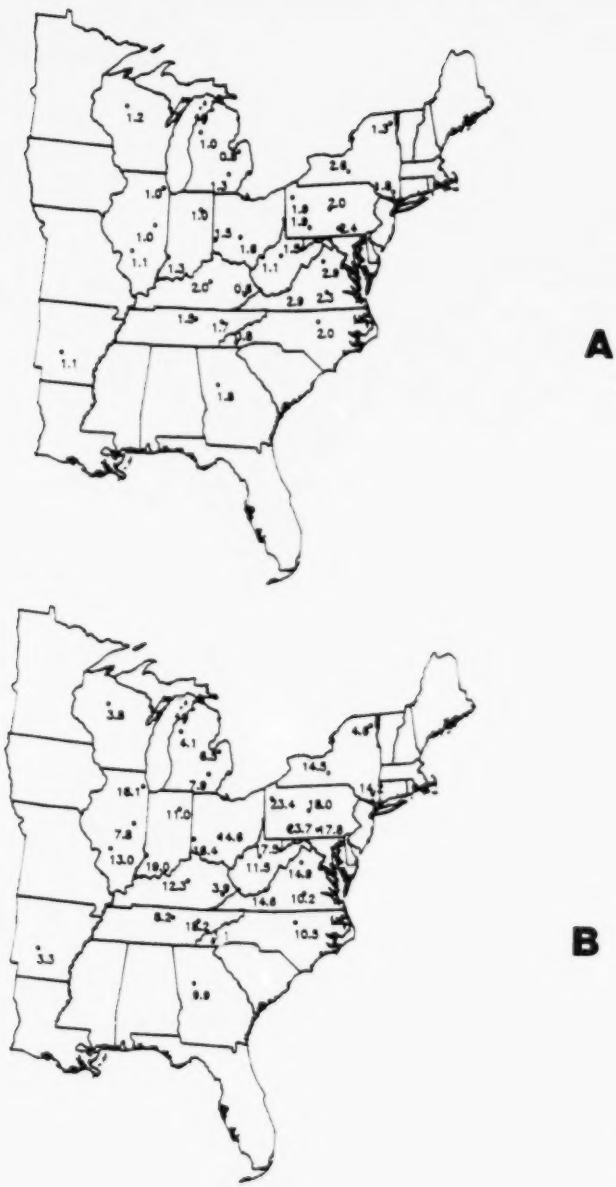

Figure 15. Average HNO_3 (A) and SO_2 (B) concentrations ($\mu g/m^3$)--fourth quarter 1988

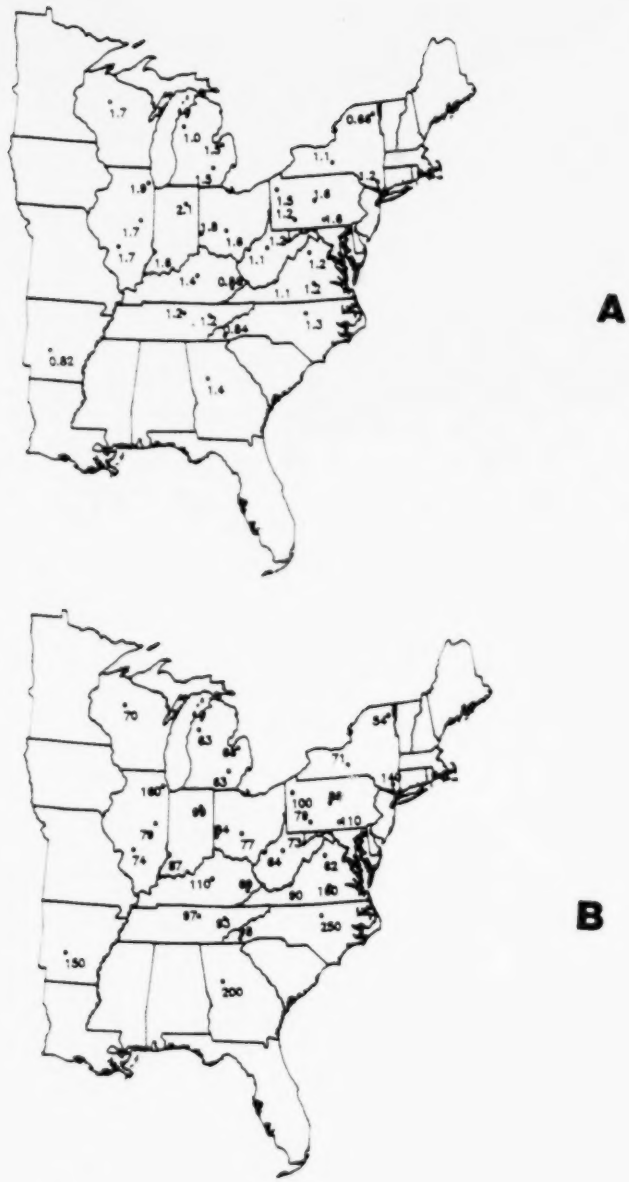

Figure 16. Average NH_4^+ (A) concentrations ($\mu g/m^3$) and Na^+ (B) concentrations (ng/m^3)--fourth quarter 1988

Figure 17. Average K^{+} (A) and Ca^{+2} (B) concentrations (ng/m^3)--fourth quarter 1988

Figure 18. Average Mg^{+2} concentrations (ng/m^3)--fourth quarter 1988

seawater (i.e., 0.248) and the assumption that all Na^+ in the sample is of marine origin. Calculations for fourth quarter 1988 indicate that marine sources account for well below 5 percent of the aerosol SO_4^{-2} observed across the NDDN.

Quarterly average K^+ concentrations show minimal variability across the network. Values range from 60 ng/m^3 at Site 105 to 210 ng/m^3 at Site 133, but are below 100 ng/m^3 at only two sites in New York state. There is little evidence of regional variability and, perhaps surprisingly, no evidence of urban influence at sites such as those located outside of Chicago (Site 146) or New York (Site 104).

Ca^{+2} data cover a wide range of concentrations, from 75 ng/m^3 at Site 105 to 2,300 ng/m^3 at Site 121. Extremely high values at the latter site are the result of coal mining traffic in the area, the impact of which is currently being investigated. In general, Ca^{+2} results show considerable site-to-site variability superimposed upon regional variability. The majority of sites in Ohio, Illinois, Indiana, and Michigan exhibit concentrations above 300 ng/m^3, whereas the remaining sites are typically well below this value. Relatively high concentrations (for northeastern sites) at Sites 107 and 120 appear to reflect nearby construction activities (now completed). Concentrations at Site 128 may be the result of local agricultural activity.

The pattern for Mg^{+2} is similar to that for Ca^{+2} and shows a combination of local and regional variability. Concentrations range from 17 ng/m^3 at Site 105 to 320 ng/m^3 at Site 146 and are almost invariably above 50 ng/m^3 in the midwest but below this figure elsewhere. This pattern presumably reflects differences in regional land use between the midwest and for other regions (i.e., agricultural versus forested). Locally high concentration of Mg^{+2} in eastern Kentucky (Site 121) appears to be due to coal mining activities.

Quarterly-average HNO_3 concentrations range from 0.6 μg/m^3 at Site 121 to 2.9 μg/m^3 at Sites 118 and 120. As for most other parameters, there is strong evidence of regional variability. In this case, the northeast exhibits generally higher concentrations than the midwest, and the southwest exhibits intermediate concentrations. A band of concentrations on the order of 2.0 μg/m^3 and above runs nearly north-south from New York to North Carolina. With the exception of Site 129 in central Kentucky and 102 in eastern Tennessee, concentrations outside of this band are less than 1.5 μg/m^3. Clearly the most dramatic feature of the HNO_3 distribution is the gradient between Sites 120 and 121. Concentration differs by nearly a factor of 5 at these sites, which are separated by only about 250 km. These two sites also present extremes in terms of local terrain. Site 120 is perched upon a mountain ridge, whereas Site 121 is nestled in a valley.

Results for SO_2 also show marked variability, both on a regional and local scale. Concentrations range from 3.1 μg/m^3 at Site 137 to 23.7 μg/m^3 at Site 117. The highest concentrations occur throughout Pennsylvania and in northern West Virginia, southern Indiana, and northern Illinois. Relatively low concentrations (i.e., <5.0 μg/m^3) occur around the periphery

of the network (Arkansas, Wisconsin, the northernmost sites in New York and Michigan) and in mountainous areas of eastern Kentucky and southeastern North Carolina. In general, the overall pattern appears similar to the geographical distribution of sources, with occasional punctuation due to possible terrain effects.

The analysis of NH_4^+ and base metal cations on Teflon® filters permits evaluation of various ionic relationships in aerosol samples. Ion balances for fourth quarter 1988 are shown in Table 6 for representative sites in the northeast, midwest, and southeast. Units of charge have been used to permit direct comparisons of ionic concentrations across species. Results show that SO_4^{-2} is the dominant anion at all sites but that the degree of dominance is less in the midwest than elsewhere. In the northeast and midwest, SO_4^{-2} typically accounts for 80 to 90 percent and 60 to 80 percent of measured anions, respectively. NH_4^+ is the dominant cation at all sites, except Site 121, and typically accounts for 70 to 80 percent of total cations. In the northeast, low concentrations of NO_3^- suggest that NH_4^+ is predominantly associated with SO_4^{-2} (or an unmeasured anion). In the midwest, in contrast, higher NO_3^- concentrations and a frequent excess of NH_4^+ over SO_4^{-2} strongly suggest the presence of NH_4NO_3. Whether this species is actually present in the atmosphere or formed as an artifact of the sampling technique is not known. Results for Ca^{+2} indicate that it is the second most abundant cation at virtually all sites and that it is more abundant in the agricultural midwest than elsewhere. Concentrations of Na^+, K^+, and Mg^{+2} are of only marginal importance to the overall ion balance. Calculations of ionic ratios based on total measured cations and anions show that reasonable balances (i.e., ±15 percent) are attained for most northeastern and southeastern sites. This suggests that the major ionic species are currently measured and that other ions (e.g., H^+ and Cl^-) play a minor role in the ionic composition of these aerosol samples. Since the database for cations is limited, it is unknown whether this is true at other times of the year. As mentioned earlier, it is also uncertain whether these results represent true atmospheric conditions or artifact reactions on Teflon® filters. Ionic balances for midwestern sites show persistent and frequently large cation excesses. These excesses correlate strongly with Ca^{+2} concentrations, suggesting that an unmeasured anion (e.g., HCO_3^- or CO_3^{-2}) is associated with this species.

Network-wide average concentrations of SO_4^{-2}, NO_3^-, HNO_3, and SO_2 are shown in Figure 19, by season, for the 18 sites in operation throughout 1988. Results for SO_4^{-2} and SO_2 exhibit dramatic differences in seasonal variability. SO_4^{-2} concentrations increase by nearly a factor of three from winter (i.e., January to March) through summer (i.e., July to September), then plummet during the fall to the lowest levels of the year. Clearly, the transition from summer to fall represents a major change in the atmospheric potential for SO_4^{-2} production. Average SO_2 concentrations, in contrast, decrease markedly from winter to summer, then return to intermediate levels in the fall.

Seasonal concentrations for NO_3^- and HNO_3 also show significant variability (see Figure 19). HNO_3 follows a similar, but less dramatic pattern as SO_4^{-2}. NO_3^- concentrations, in contrast, more than double from

TABLE 6. AEROSOL ION BALANCES FOR FOURTH QUARTER 1988

Region	State	Site	Anions (neq/m^3)		Cations (neq/m^3)					Cations/ Anions	NH_4^+ / Cations	SO_4^{-2} / Anions
			SO_4^{-2}	NO_3^-	NH_4^+	Na^+	K^+	Ca^{+2}	Mg^{+2}			
Northeast	NY	104	71	10	67	6	2	8	4	1.07	0.77	0.88
	NY	105	48	5	37	2	2	4	1	0.87	0.80	0.91
	PA	117	77	9	67	3	3	10	2	0.99	0.79	0.90
	PA	128	77	29	89	5	3	17	4	1.11	0.75	0.73
	WV	119	67	9	61	3	3	8	2	1.01	0.79	0.88
	VA	120	79	13	61	4	4	17	4	0.98	0.74	0.86
	VA	108	75	7	67	7	3	6	3	1.05	0.78	0.91
Midwest	MI	149	50	16	56	3	3	8	3	1.11	0.77	0.76
	OH	114	73	34	89	3	3	21	7	1.15	0.72	0.68
	IN	133	77	55	117	4	5	29	10	1.25	0.71	0.58
	IL	130	69	47	94	3	5	46	12	1.38	0.59	0.59
	KY	121	60	11	48	3	4	115	10	2.53	0.27	0.85
	KY	129	73	24	78	5	3	18	4	1.11	0.80	0.75
Southeast	NC	101	83	14	72	11	4	8	1	0.99	0.75	0.86
	NC	137	60	4	47	4	3	4	1	0.92	0.80	0.94
	TN	127	69	14	67	4	3	16	3	1.12	0.72	0.83
	TN	102	83	13	67	4	4	16	5	1.00	0.70	0.86
	GA	153	75	11	78	9	4	8	3	1.19	0.76	0.87

Note: neq/m^3 = nanoequivalents per cubic meter.

Source: Hunter/ESE, 1989.

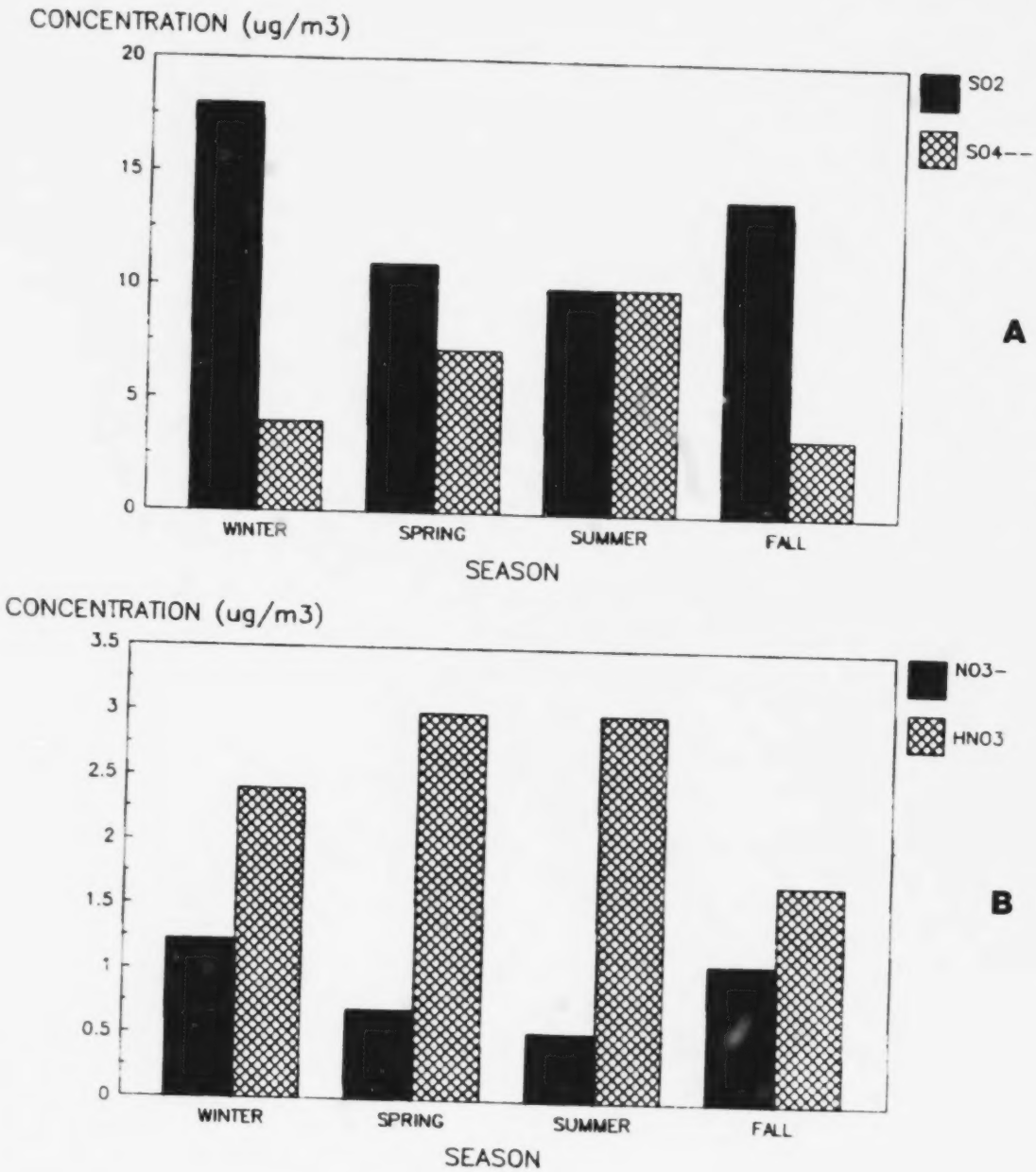

Figure 19. Network-wide concentrations of SO_4^{-2}/SO_2 (A) and NO_3^-/HNO_3 (B) by season

summer to winter, perhaps due to the temperature-dependent equilibrium between aerosol NH_4NO_3 and gas phase HNO_3 and NH_3.

4.1.3 Day Versus Night Concentration Data

Day and night filter pack samples were collected during 1988 to determine whether diurnal variations existed which could affect the uncertainty of dry deposition estimates. Results are summarized here for four sites that are representative of the major terrain classifications within the network. Data from these sites exemplify the day/night variability observed throughout the network.

Day/night concentrations of SO_4^{-2} and SO_2 for sites in central Illinois (Site 130), central Kentucky (Site 129), eastern Kentucky (Site 121), and southwestern Virginia (Site 120) are compared by quarter in Table 7. Results for SO_4^{-2} show differences of less than 20 percent between day and night for all sites and all times of the year. Data for Site 130, which is located in prime agricultural flatland, show a consistent decrease in concentration of approximately 10 percent from day to night. For Site 129 in rolling terrain, day/night concentrations are virtually identical during quarters one and four and show a 10-percent decrease during the middle two quarters of the year. Day/night concentrations at Site 121 (complex terrain) are similar during first and fourth quarters and show nocturnal depressions of 10 and 20 percent, respectively, during second and third quarters. Site 120 (mountaintop) is unique in that day/night concentrations are invariant throughout the year.

The diurnal variability of SO_2 is much more pronounced than that of SO_4^{-2} and apparently more dependent upon terrain and season. Nocturnal concentrations at Site 130 are 10, 25, and 35 percent lower than daytime values during second, third, and fourth quarters, respectively. At Site 129, nocturnal concentrations are reduced by up to 25 percent during quarters one and four and by 33 percent during quarters two and three. Site 121 shows dramatic day/night differences. Night concentrations are reduced by 40 to 50 percent during first and fourth quarters and show nearly total depletion during quarters two and three. As was observed for SO_4^{-2}, Site 120 shows no evidence of significant day/night variability. Examination of SO_2 data across Sites 129, 121, and 120 suggests that nocturnal depletion could explain some, but not all, of the annual and seasonal spatial variability described previously.

Results for NO_3^- show unique patterns of day/night variability (see Table 8). For Sites 129 and 120, differences between day and night are small but generally suggest slightly higher concentrations at night than during the day. At Site 121, differences are also small but suggest slightly higher concentrations during the day. Results for Site 130 show substantially higher nighttime concentrations during all three seasons that the site was in operation. Although these data suggest nocturnal production of NO_3^- aerosol at certain sites, it should be noted that artifact reactions on filter media could also account for these patterns. For example, HNO_3 may be scavenged by wetted Teflon® filters at high relative humidity, periods of which occur frequently at night.

TABLE 7. DAY VERSUS NIGHT CONCENTRATIONS OF SO_4^{-2} AND SO_2 ($\mu g/m^3$) BY QUARTER FOR 1988

Site	Terrain Classification	Sample Period	SO_4^{-2} 1	2	3	4	SO_2 1	2	3	4
130	Flat	Day	N/O	6.9	9.2	3.6	N/O	10.2	10.6	10.2
		Night	N/O	6.3	8.5	3.2	N/O	9.1	8.1	6.7
129	Rolling	Day	4.5	11.0	12.4	3.6	21.2	17.1	11.0	13.7
		Night	4.4	9.8	11.1	3.5	18.4	11.5	7.4	10.3
121	Complex	Day	3.9	8.2	10.4	3.0	9.2	7.8	4.7	5.2
		Night	3.7	7.6	8.6	2.8	5.4	1.1	0.4	2.6
120	Mountaintop	Day	4.1	9.2	11.4	3.7	15.2	8.9	8.4	13.0
		Night	4.2	9.6	11.0	3.7	15.7	9.5	7.6	13.4

Note: 1, 2, 3, and 4 refer to first, second, third, and fourth quarters, respectively.
N/O = not operational.

Source: Hunter/ESE, 1989.

TABLE 8. DAY VERSUS NIGHT CONCENTRATIONS OF NO_3^- AND HNO_3 ($\mu g/m^3$) BY QUARTER FOR 1988

Site	Terrain Classification	Sample Period	NO_3^- 1	NO_3^- 2	NO_3^- 3	NO_3^- 4	HNO_3 1	HNO_3 2	HNO_3 3	HNO_3 4
130	Flat	Day	N/O	1.1	1.1	2.4	N/O	5.7	5.4	1.3
		Night	N/O	1.5	1.6	3.3	N/O	3.0	2.4	0.7
129	Rolling	Day	1.0	0.7	0.5	1.4	3.6	6.3	5.2	2.2
		Night	1.3	0.8	0.6	1.5	3.1	3.4	2.6	1.6
121	Complex	Day	1.2	0.5	0.3	0.8	1.4	2.6	2.2	0.8
		Night	1.1	0.4	0.2	0.6	0.6	0.6	0.3	0.7
120	Mountaintop	Day	0.7	0.6	0.4	0.7	3.2	4.2	4.1	2.6
		Night	1.0	0.8	0.3	0.9	3.9	4.2	3.1	3.0

Note: 1, 2, 3, and 4 refer to first, second, third, and fourth quarters, respectively.
N/O = not operational.

Source: Hunter/ESE, 1989.

HNO_3 data show significant nocturnal depletion for most seasons at Sites 121, 129, and 130. As with SO_2, HNO_3 nearly vanishes during the night at Site 121, especially during second and third quarters. Reductions at Sites 129 and 130 are close to 50 percent over the same period. In contrast, results for Site 120 exhibit only small decreases, if any, during second and third quarters and small but statistically significant increases during first and fourth quarters. As noted for NO_3^-, artifact reactions may confound interpretation of HNO_3 data. For example, nocturnal depletion of HNO_3 and enhancement of NO_3^- at Site 130 could be explained, in part, by phase changes on the Teflon® filter. At the remaining sites, however, calculations of total NO_3^- (i.e., HNO_3 plus NO_3^-) support observations of significant nocturnal depletion during the second and third quarters.

4.2 OZONE

Daily average and daily maximum O_3 concentrations for sites that were operational throughout 1988 are shown in Figures 20 through 28. Each figure also shows a horizontal line at 120 ppb, which represents the National Ambient Air Quality Standard (NAAQS) for O_3. In general, results for all sites reflect the classical seasonal cycle of O_3 production. Maximum concentrations are observed during the period June through September and minimum concentrations are observed in November, December, and January. Seasonal variability of this nature has been observed previously over widespread areas of the eastern United States (Altshuller, 1987; Meagher et al., 1987).

Inspection of daily O_3 averages for 1988 shows that there is considerable fine structure in the overall annual pattern. O_3 concentrations at nearly all sites rise and decay with a period of approximately 5 to 10 days, which is probably meteorologically driven. Examination of daily maxima shows that approximately 75 percent of the 1988 O_3 values greater than or equal to 100 ppb occurred during four such oscillations: May 28 through June 1; June 13 through June 17; July 3 through July 9; and August 16 through August 19. Maximum hourly O_3 concentrations observed during these four periods are shown for each site in Figures 29 and 30.

Results for the period May 28 through June 1 show maximum O_3 values that frequently differ between sites by little more than the instrumental uncertainty. Maximum concentrations range from 81 ppb in southwestern North Carolina (Site 137) to 204 ppb in southeastern New York (Site 103/4) but are between 110 and 125 ppb in all states except Kentucky and Tennessee.

Data for the period June 13 through June 17 also exhibit the highest and lowest concentrations at Sites 103/4 and 137, respectively. The region of highest concentrations (i.e., >110 ppb) is somewhat contracted, relative to the previous episode, and there is considerable patchiness along the flanks of the Appalachian Mountains. For many sites, the highest hourly average concentration of the year was observed during the period July 3 through July 9. Maximum hourly concentrations for the episode ranged from

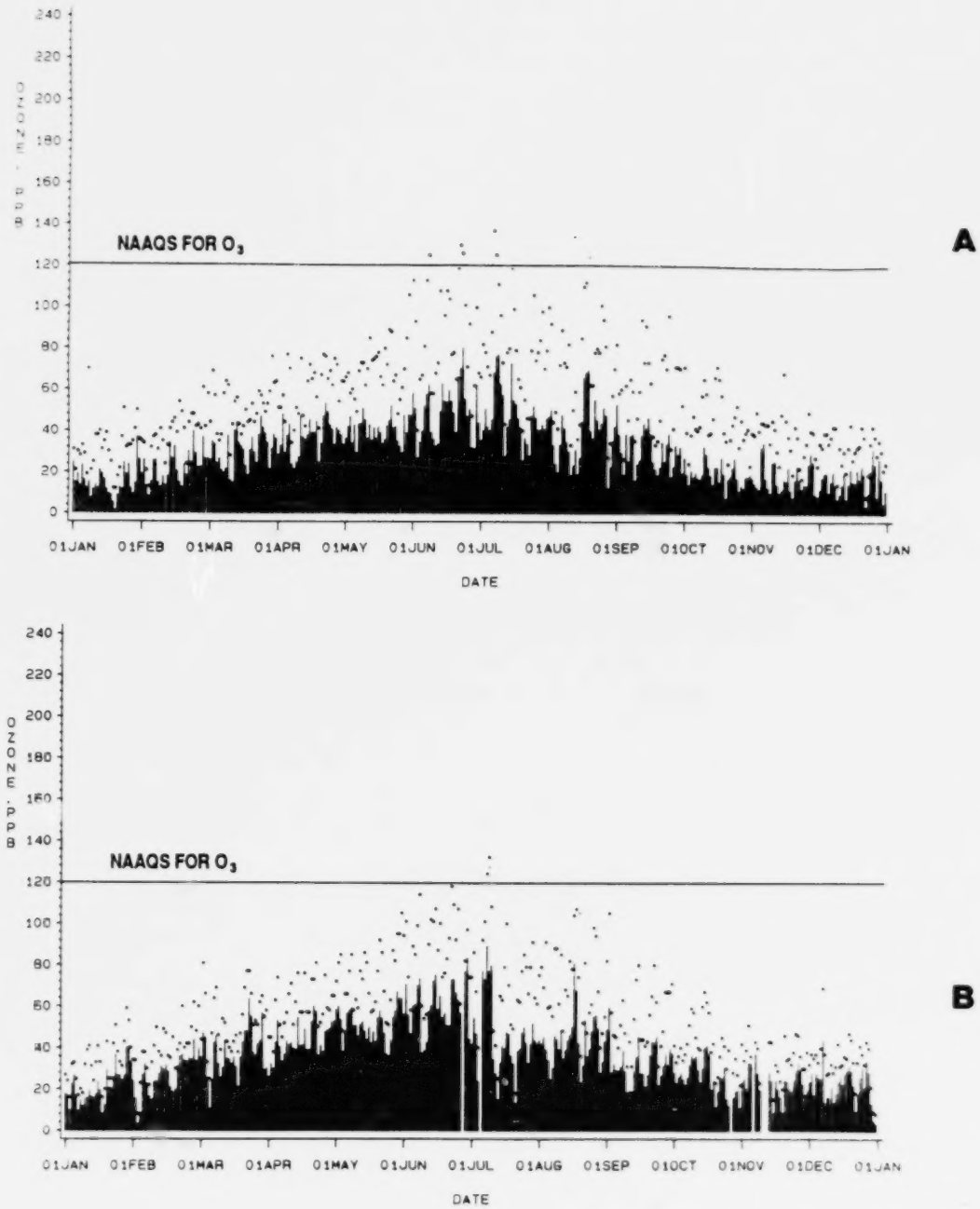

Figure 20. O_3 daily averages and maxima for Sites 101 (A) and 102 (B)--1988

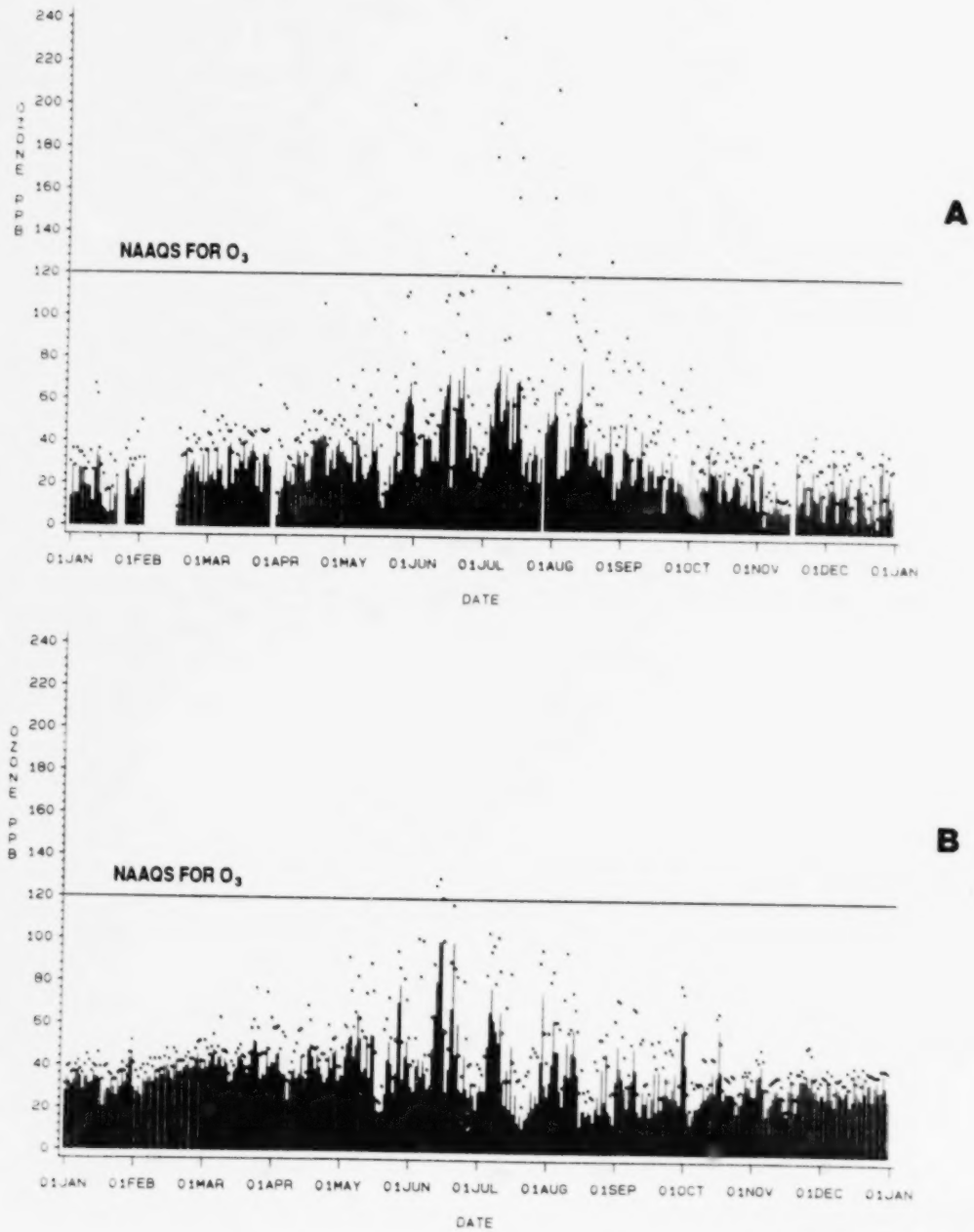

Figure 21. O_3 daily averages and maxima for Sites 103/4 (A) and 105 (B)--1988

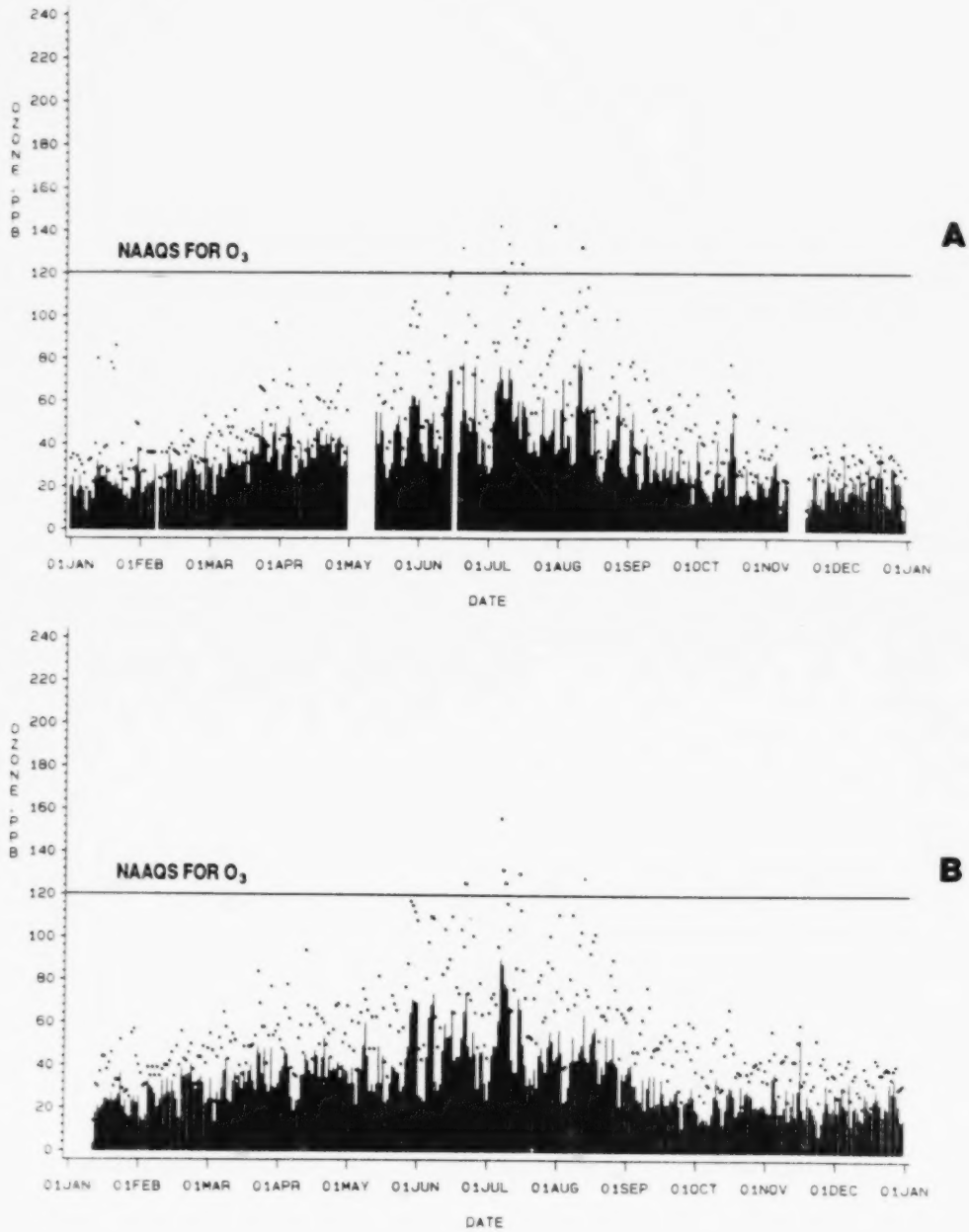

Figure 22. O_3 daily averages and maxima for Sites 106 (A) and 107 (B)--1988

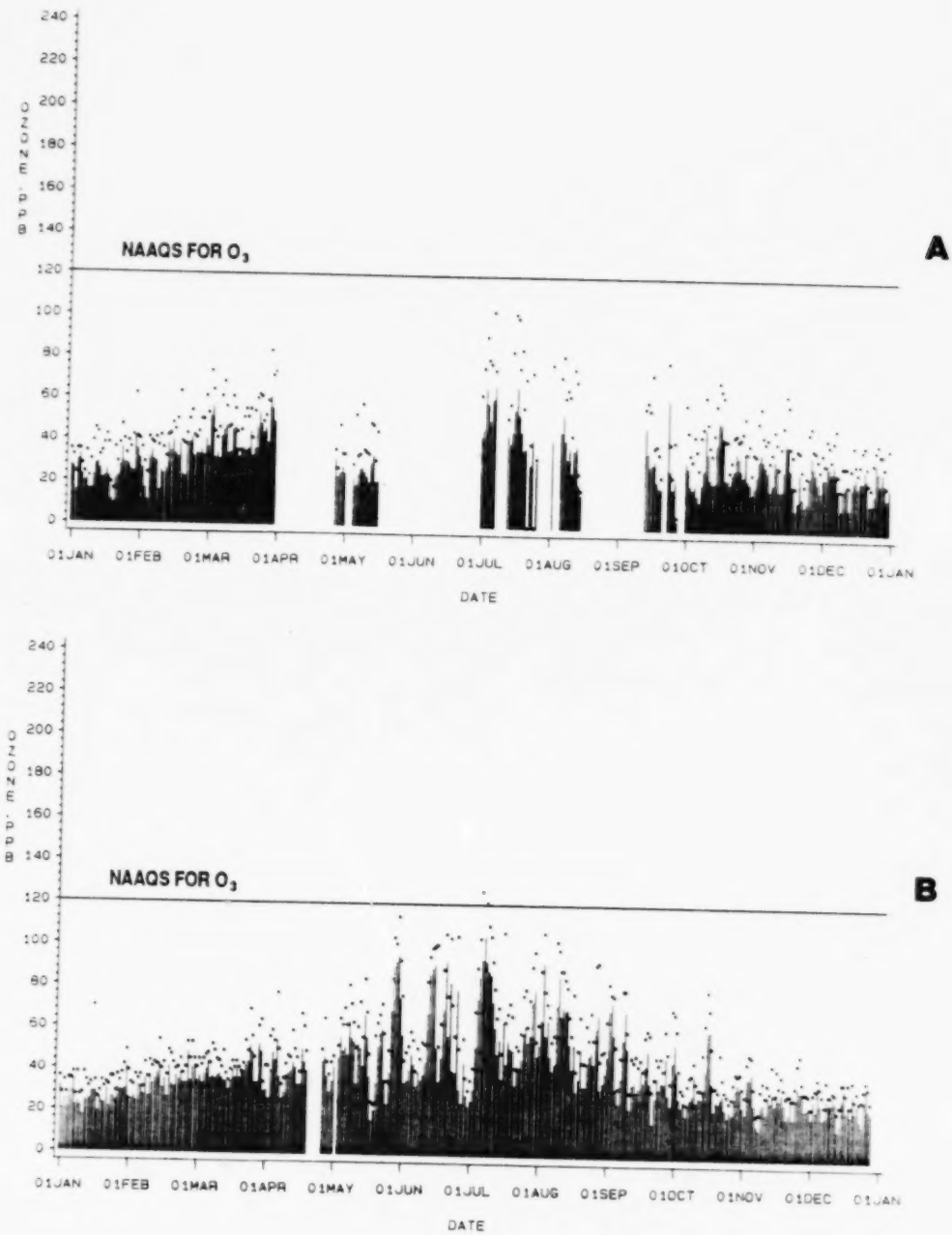

Figure 23. O_3 daily averages and maxima for Sites 108 (A) and 110 (B)--1988

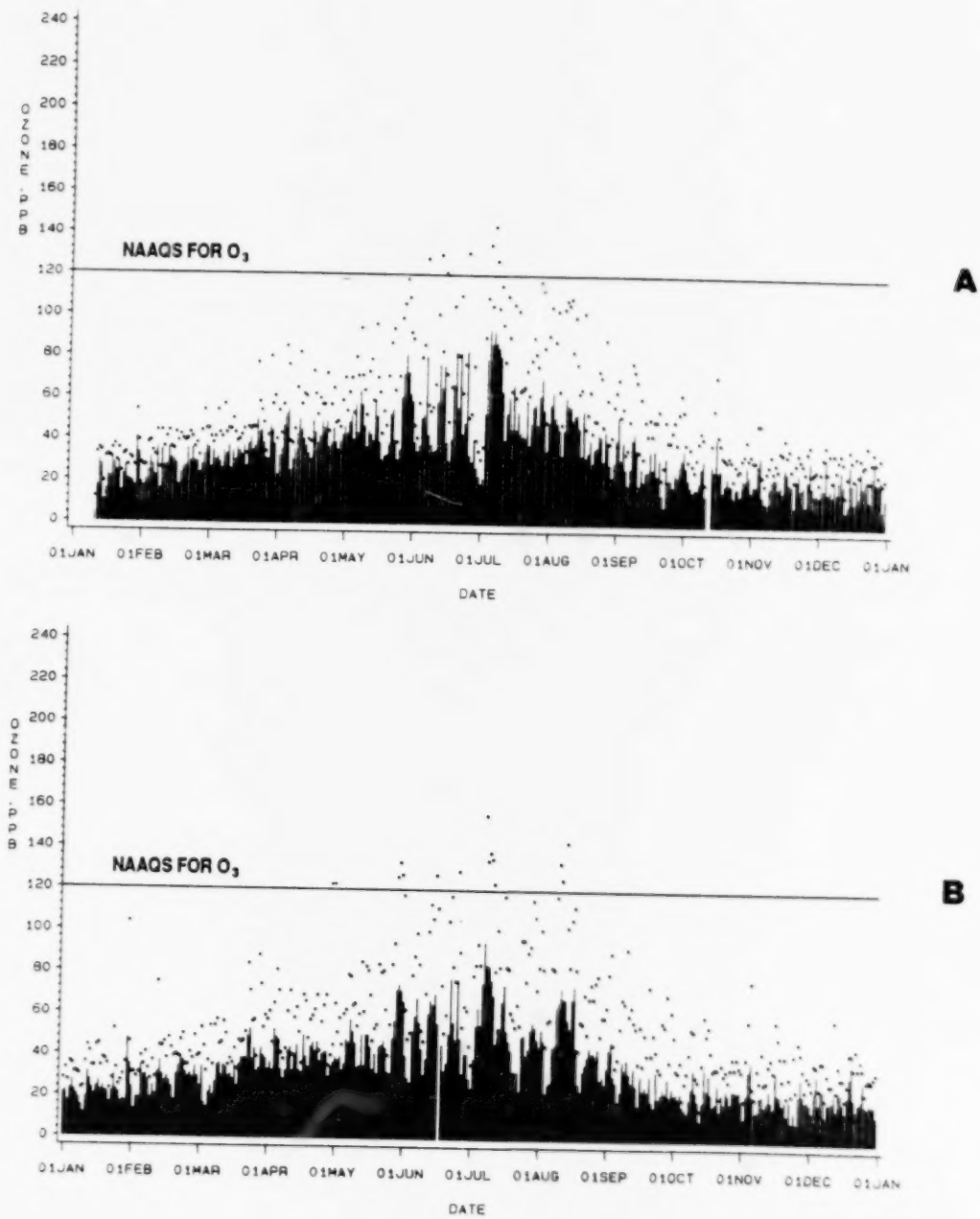

Figure 24. O_3 daily averages and maxima for Sites 113 (A) and 117 (B)--1988

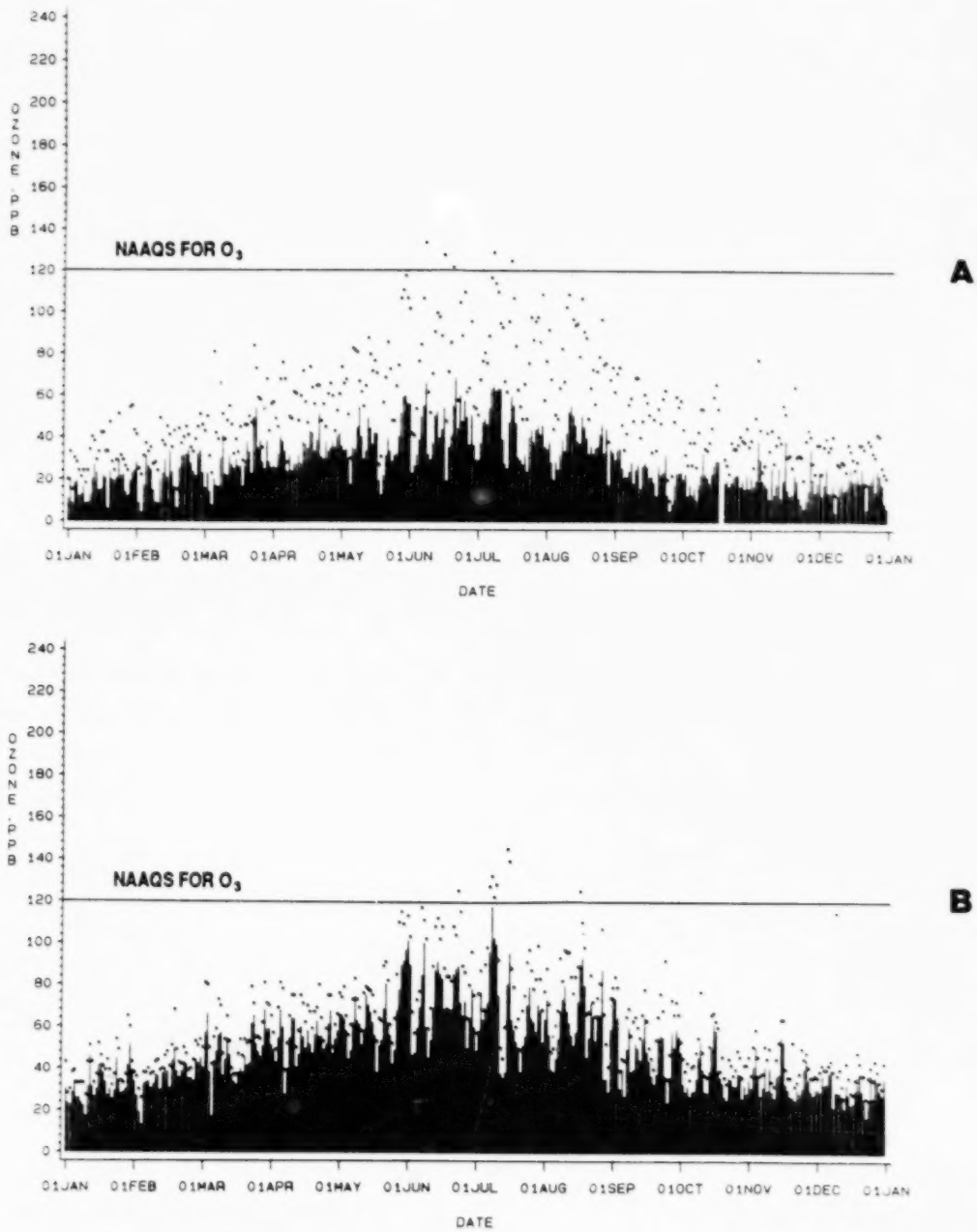
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Figure 25. O_3 daily averages and maxima for Sites 119 (A) and 120 (B)--1988

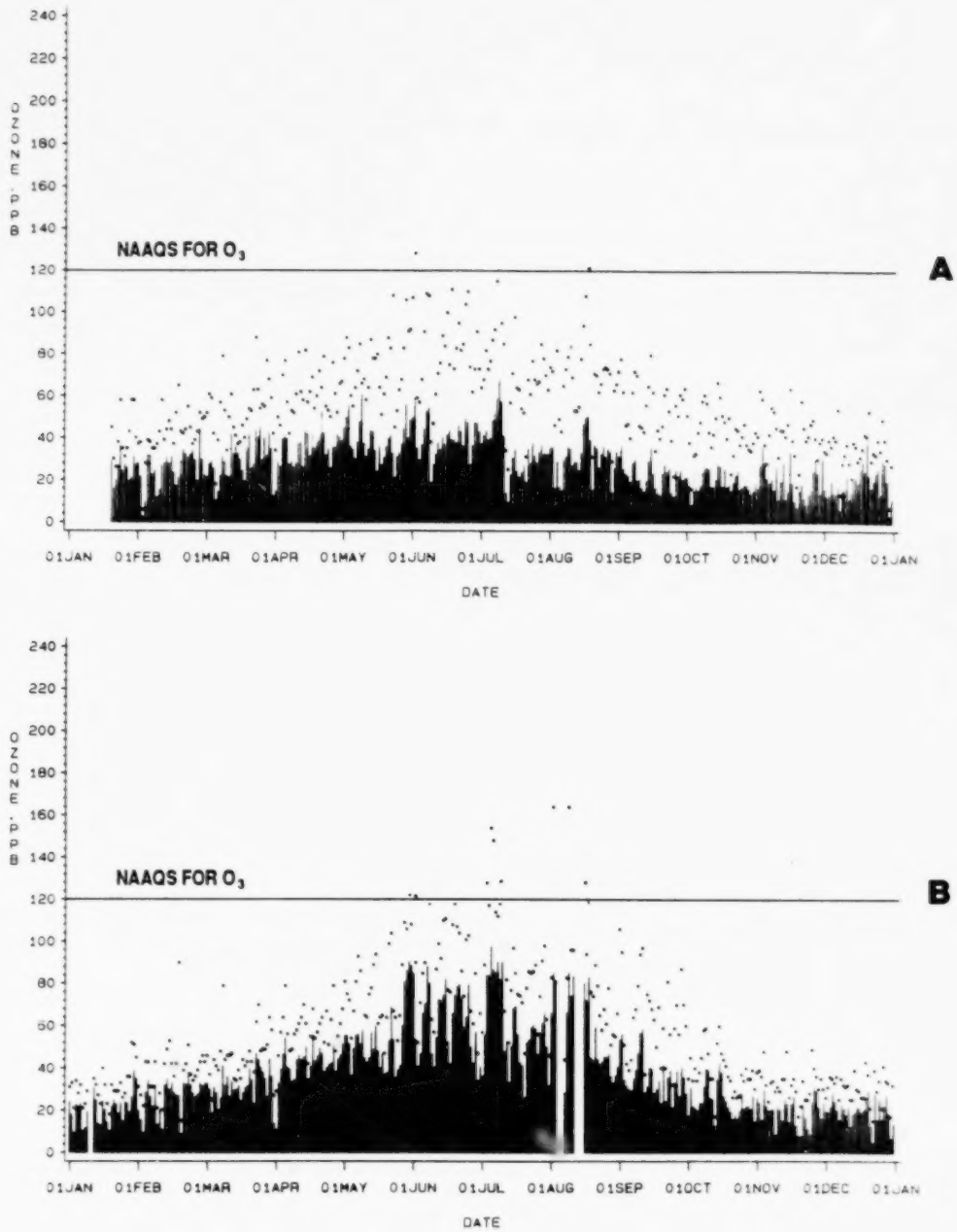

Figure 26. O_3 daily averages and maxima for Sites 121 (A) and 122 (B)--1988

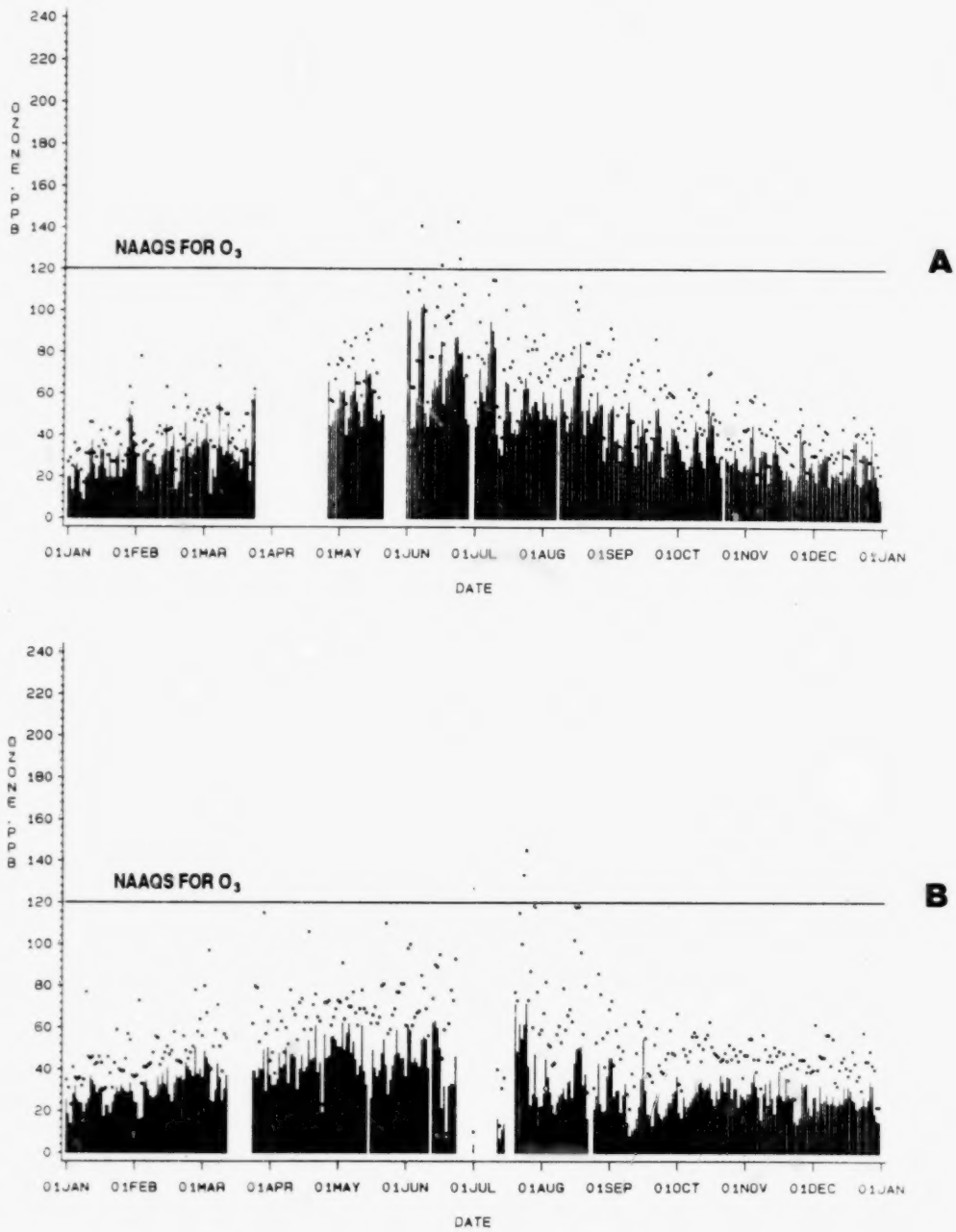

Figure 27. O_3 daily averages and maxima for Sites 129 (A) and 137 (B)--1988

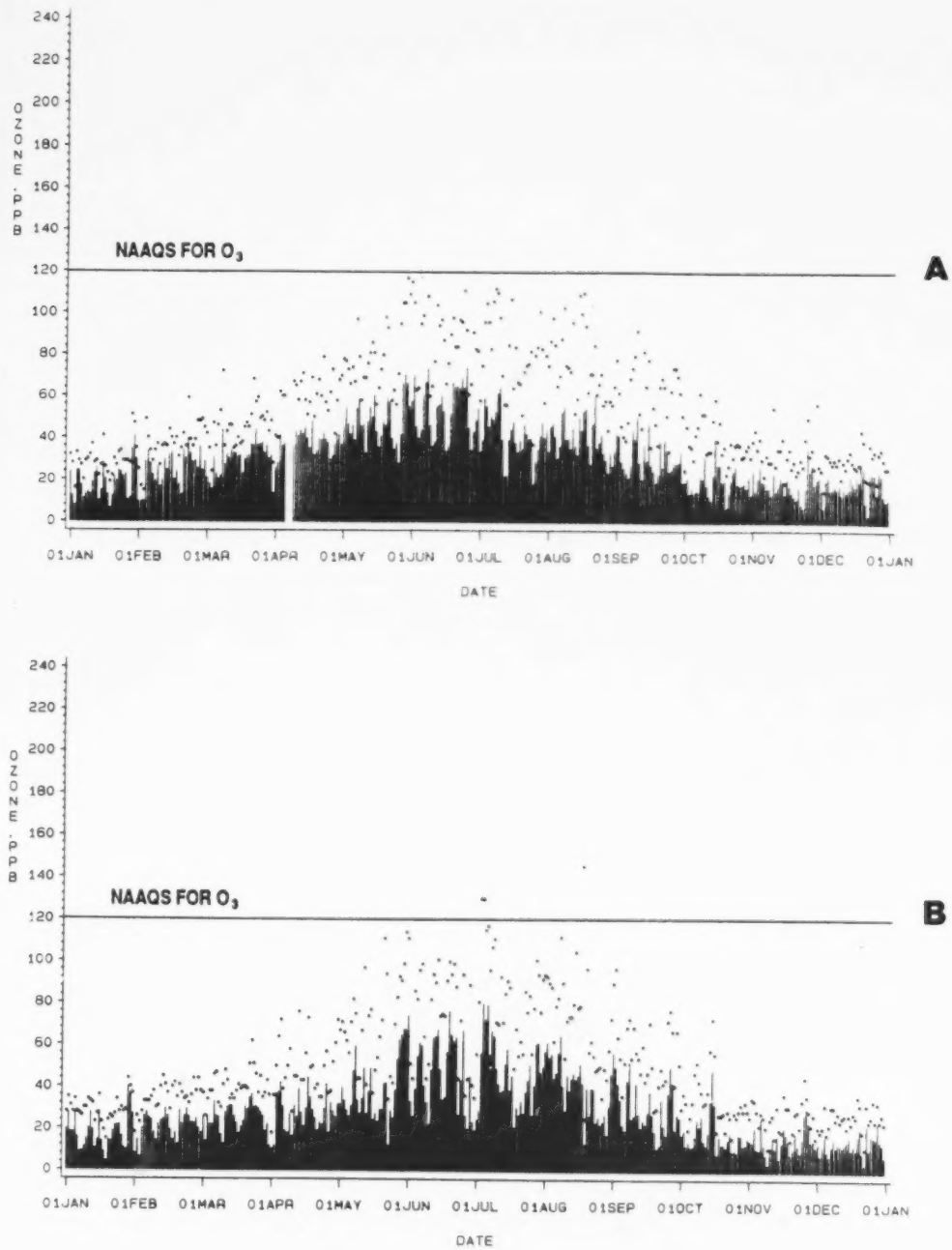
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Figure 28. O_3 daily averages and maxima for Sites 140 (A) and 146 (B)--1988

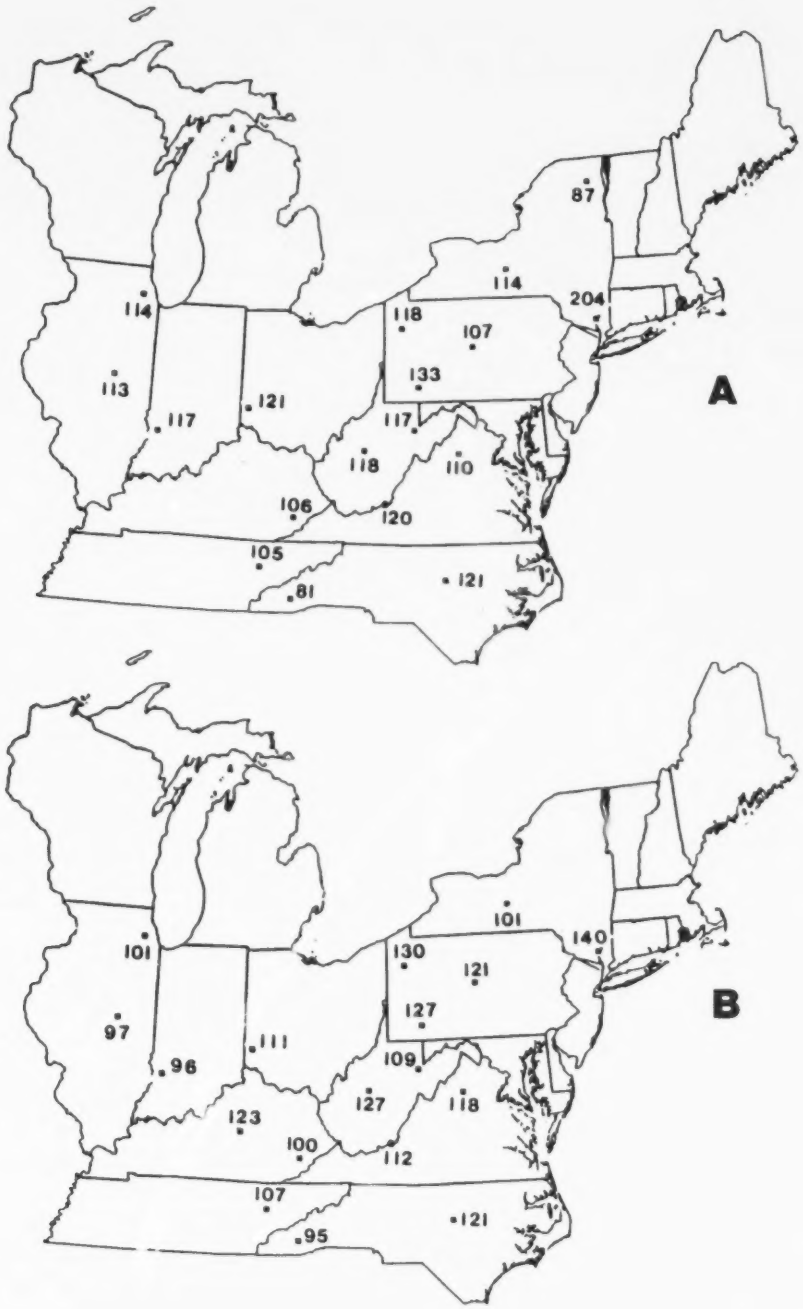


Figure 29. Maximum hourly O_3 (ppb) for May 28 - June 1, 1988 (A) and June 13 - June 19, 1988 (B)

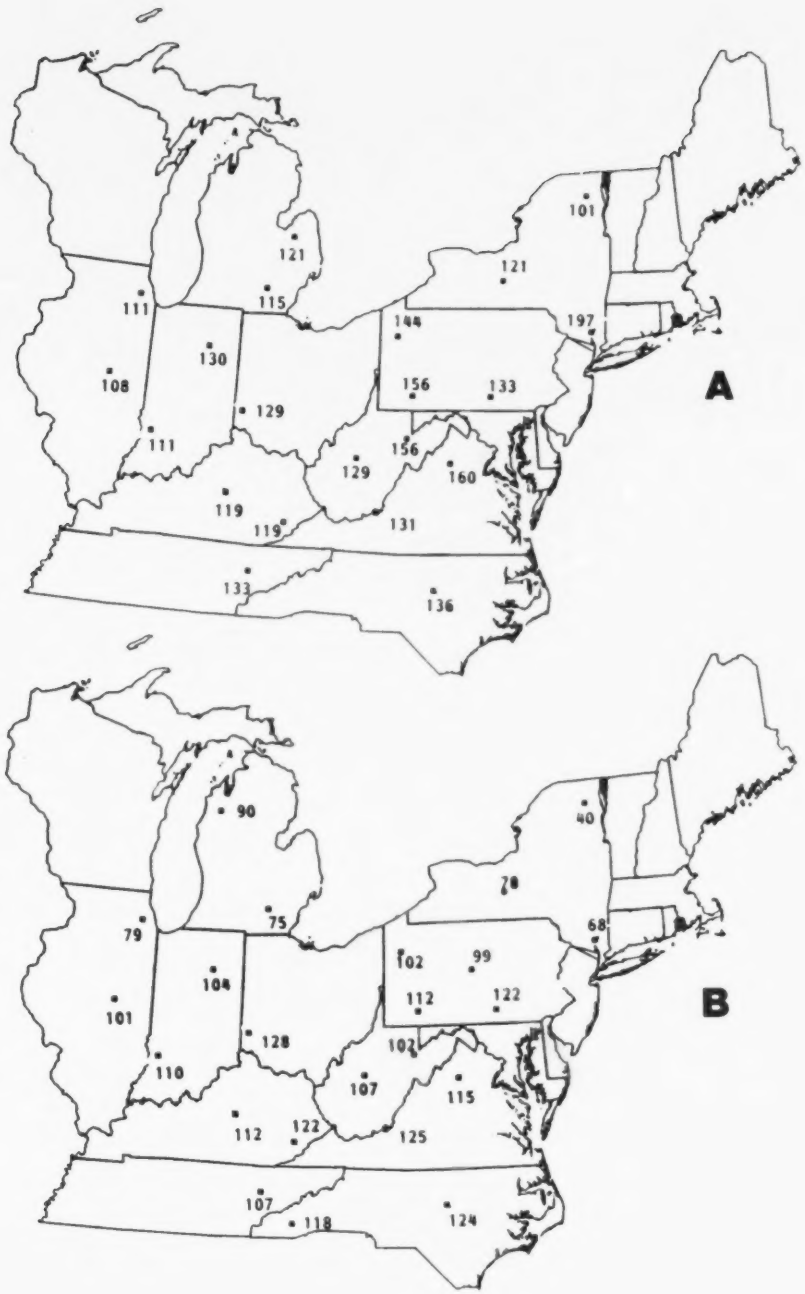


Figure 30. Maximum hourly O_3 (ppb) for July 3 - July 9, 1988 (A) and August 16 - August 19, 1988 (B)

197 ppb in southeastern New York (Site 104) to 101 ppb in extreme northern New York. A region of concentrations in excess of 125 ppb extended from northern Indiana to New York and southward (excluding Kentucky) to Tennessee and North Carolina. As with previous episodes, the two sites in Illinois appear to be along the fringe of the region of elevated concentrations.

The episode of August 16 through 19 shows a fairly dramatic latitudinal gradient in maximum concentrations. Maximum hourly values were well below 100 ppb across New York, Michigan, and northern Illinois, roughly 100 ppb across central Pennsylvania, northern Indiana, and central Illinois, and well above 100 ppb (except for one site in West Virginia) at all remaining sites. Relatively low concentrations in New York, Michigan, and Illinois appear to be due to a stationary front, which brought widespread cloudiness and scattered rainfall to the northern extremes of the network.

Synoptic meteorological conditions during the four O_3 episodes were generally very similar. A stagnating high pressure system covered the region, bringing high temperatures, clear skies, and light and variable winds. Precipitation was nearly absent, except for isolated thunderstorms in the southeast. In most cases, episodes were terminated by the incursion of a cold front and associated precipitation.

Although peak concentrations of O_3 were reasonably constant from site to site during the July 3 through 9 episode, the same does not apply for time-averaged values. Figure 31 shows the diurnal evaluation of O_3 for three sites extending from central Kentucky to southwestern Virginia. The central Kentucky site (Site 129) is located in an open meadow in rolling terrain; the eastern Kentucky site (Site 121) is located in a valley in complex terrain; and the Virginia site (Site 120) is located on a mountaintop at an elevation of 972 m. Time series data for these sites show marked differences in the temporal behavior of O_3. The mountaintop site shows a day-to-day increase in O_3 concentrations but little evidence of day/night variability. The open meadow site shows significant decay of O_3 from mid-day highs to early morning lows. For the days shown, the early morning low is in the range of 40 to 60 ppb and roughly 50 percent of the previous peak. The complex terrain site shows an extremely pronounced day/night pattern. Daytime maxima increase steadily throughout the episode while nighttime minima show nearly complete O_3 depletion on all but the last day.

One explanation for this behavior involves the relationship between sampler location and the nocturnal inversion layer. The mountaintop site presumably sits above the inversion layer and, therefore, is always in contact with a large reservoir for O_3. The rolling terrain and complex terrain site lies below the inversion layer, within which O_3 is subject to a variety of depletion processes. Longer lasting and/or shallower inversions could result in more rapid decay of O_3 in complex terrain than in rolling terrain. The end result of this day/night variability is a gradient in integrated exposure (i.e., average concentrations) from mountaintop to rolling terrain to complex terrain. Although there is no

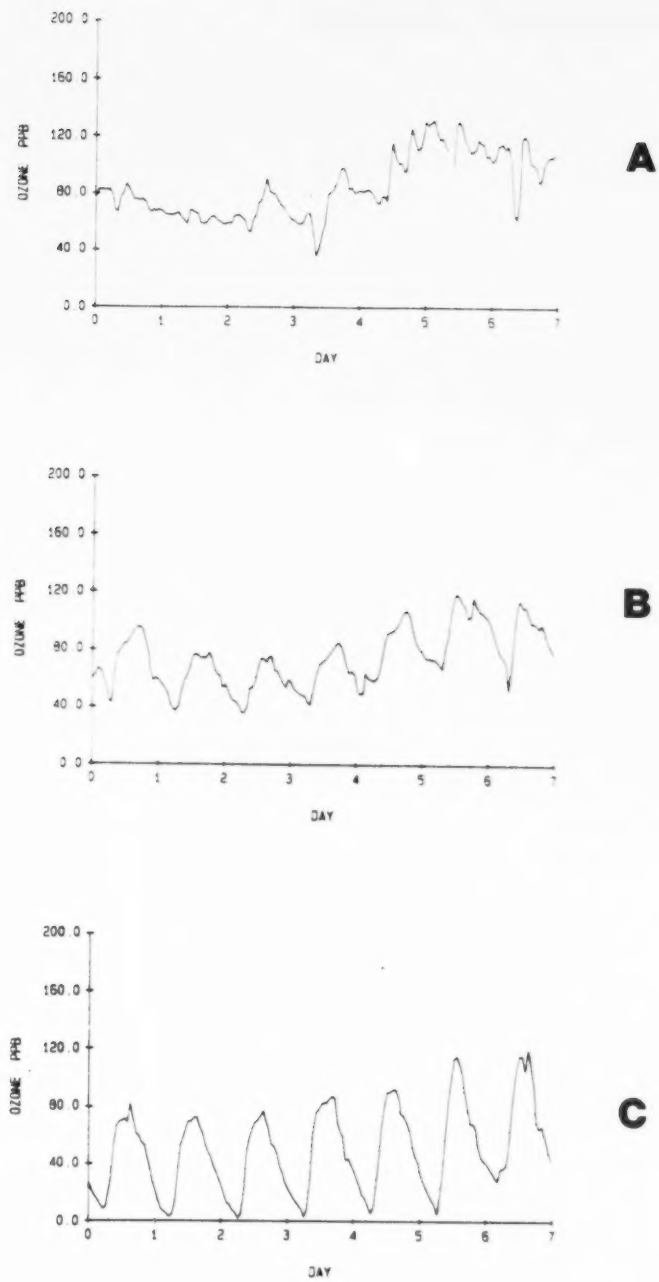


Figure 31. O_3 time series for Site 120 (A), Site 129 (B), and Site 121 (C) for July 3 - July 9, 1988

continuous data to support this, the same terrain effect might also account for the SO_2 and HNO_3 pattern described previously for these sites (see Figure 7).

4.3 SUMMARY OF METEOROLOGICAL OBSERVATIONS

Meteorological data are gathered at each site to satisfy input requirements for one or more dry deposition algorithms. These algorithms produce hourly deposition velocities (based on field observations) which are then averaged over weekly periods and merged with concentration data to calculate fluxes. The hourly meteorological data for 1988 have been submitted to EPA and are far too voluminous to evaluate in this report. The purpose of this section is to present quarterly averages for meteorological parameters and annual wind roses for the network. The sources of data for this section are 18 sites, which were operational throughout 1988.

Quarterly average values for temperature, relative humidity, and solar radiation are shown in Table 9. Sites have been organized by region (i.e., southeast, midwest, and northeast) in order to facilitate identification of large-scale patterns, if they exist. Results generally conform to the expected seasonal patterns of temperature, relative humidity, and solar radiation. Comparison of values across regions, however, show that the midwest was relatively hot, dry, and sunny, especially during the second and third quarters. This apparently reflects the extreme drought, which parched much of the midwest during 1988. Data for second quarter 1988 indicate that relative humidity and solar radiation were as much as 20 percent lower and 20 percent higher, respectively, in the midwest than the northeast.

Data for windspeed, wind direction, and sigma theta (the standard deviation of wind direction) are listed by quarter in Table 10. Results for windspeed and wind direction show appreciable seasonality across all regions. In general, windspeeds decrease markedly from first through third quarters, then pick up again during fourth quarter. Wind direction backs from approximately southwest to south during the first half of the year and then veers to southwest through the second half of the year. Dramatic differences between sites are apparent for windspeed and sigma theta. As a rule, these differences correlate well with terrain classification. Windspeeds are highest and sigma theta lowest in flat or rolling terrain, such as at Site 130, while the converse is true for sites in complex terrain such as Site 121. Based on the 1988 data set, representative sigma theta values for flat, rolling, and complex terrain sites are on the order of 10 to 20 degrees, 20 to 30 degrees, and 40 to 55 degrees, respectively. Windspeed and sigma theta are important variables for characterization of gas phase resistance in a variety of dry deposition algorithms (Hicks et al., 1988; Wesley and Lesht, 1988). Terrain-dependent values for these parameters may, therefore, produce appreciable differences in deposition velocity between sites.

Annual plots of windspeed and wind direction are shown in Figures 32 through 40. As discussed earlier, there are similarities among sites in

TABLE 9. QUARTERLY AVERAGE TEMPERATURE, RELATIVE HUMIDITY, AND SOLAR RADIATION DURING 1988

Region	State	Site	Temperature (°C)				Relative Humidity (%)				Solar Radiation (W/m^2)			
			1	2	3	4	1	2	3	4	1	2	3	4
Northeast	NY	104	-1.7	13.3	19.8	2.5	71	70	76	73	114	208	199	80
	NY	105	-5.8	10.6	17.1	-0.6	60	63	69	73	97	195	180	60
	NY	110	-3.2	12.4	18.0	2.0	66	61	63	68	96	231	214	70
	PA	106	-1.0	13.9	20.0	3.9	69	66	INS	65	111	214	204	88
	PA	113	-1.1	13.0	19.2	5.0	67	63	INS	74	106	235	216	86
	PA	117	-2.2	12.3	18.2	2.5	69	66	75	73	92	209	201	76
	WV	107	1.2	13.8	20.1	4.4	70	67	74	71	114	223	INS	78
	WV	119	1.1	15.0	20.9	4.7	82	76	78	73	87	220	202	79
	VA	108	3.6	INS	INS	7.9	54	INS	INS	57	156	INS	INS	100
	VA	120	0.7	14.5	19.6	4.6	68	67	78	71	131	244	INS	102
Midwest	IL	130	INS	18.9	22.8	4.2	INS	49	65	73	INS	271	238	INS
	IL	146	-3.1	15.8	22.4	3.3	71	49	59	70	101	233	213	88
	IN	140	1.2	19.0	23.7	6.3	66	48	65	67	125	295	239	104
	OH	122	0.0	16.8	22.1	4.8	67	50	62	68	118	269	278	INS
	KY	121	4.4	15.3	21.1	6.0	65	68	74	74	122	237	199	93
	KY	129	1.2	INS	23.1	7.2	66	INS	70	66	111	INS	213	105
Southeast	TN	102	4.9	18.4	23.1	8.4	58	57	67	61	124	221	199	105
	NC	101	6.0	18.2	24.3	9.0	65	68	75	69	133	243	211	122
	NC	137	3.3	14.8	19.5	6.5	70	68	86	75	134	259	INS	INS

Note: INS = insufficient data completeness (i.e., less than 75-percent for quarter).

Source: Hunter/ESE, 1989.

TABLE 10. QUARTERLY AVERAGE WINDSPEED, WIND DIRECTION, AND SIGMA THETA DURING 1988

Region	State	Site	Wind Speed (m/s)				Wind Direction (°)				Sigma Theta (°)			
			1	2	3	4	1	2	3	4	1	2	3	4
Northeast	NY	104	1.7	1.6	1.0	1.6	238	215	215	236	2	4	3	2
	NY	105	1.6	1.1	0.8	1.0	221	203	234	221	51	49	52	54
	NY	110	2.0	1.7	1.2	1.8	233	231	223	232	32	36	43	36
	PA	106	2.9	3.0	1.9	3.3	218	197	205	228	20	21	26	20
	PA	113	3.1	2.4	1.6	3.5	212	200	179	210	15	19	23	17
	PA	117	1.1	0.8	0.7	1.0	193	188	207	196	47	49	45	47
	WV	107	2.2	2.0	1.5	2.1	250	233	212	243	26	29	34	28
	WV	119	1.1	0.9	0.6	0.8	206	198	177	190	35	39	42	39
	VA	108	2.3	INS	INS	1.8	198	INS	INS	195	19	INS	INS	21
	VA	120	3.8	2.6	2.1	3.5	255	240	218	253	21	24	25	13
Midwest	IL	130	INS	4.8	3.0	5.1	INS	175	177	220	INS	13	17	7
	IL	146	3.7	3.1	2.4	3.4	214	157	191	231	11	15	17	12
	IN	140	3.0	2.2	1.4	2.6	206	169	168	205	20	29	33	23
	OH	122	2.4	2.0	1.1	2.0	205	180	187	212	24	27	32	12
	KY	121	0.5	0.5	0.4	0.5	232	240	252	250	54	41	39	50
	KY	129	3.7	INS	2.0	3.4	212	INS	186	201	11	INS	16	10
Southeast	TN	102	1.0	0.7	0.6	1.0	209	181	126	INS	37	47	46	INS
	NC	101	1.9	1.8	1.7	1.7	184	189	168	187	22	26	25	25
	NC	137	0.8	0.7	0.4	0.6	191	209	208	205	52	51	49	53

Note: INS = insufficient data completeness (less than 75-percent for quarter).

Source: Hunter/ESE, 1989.

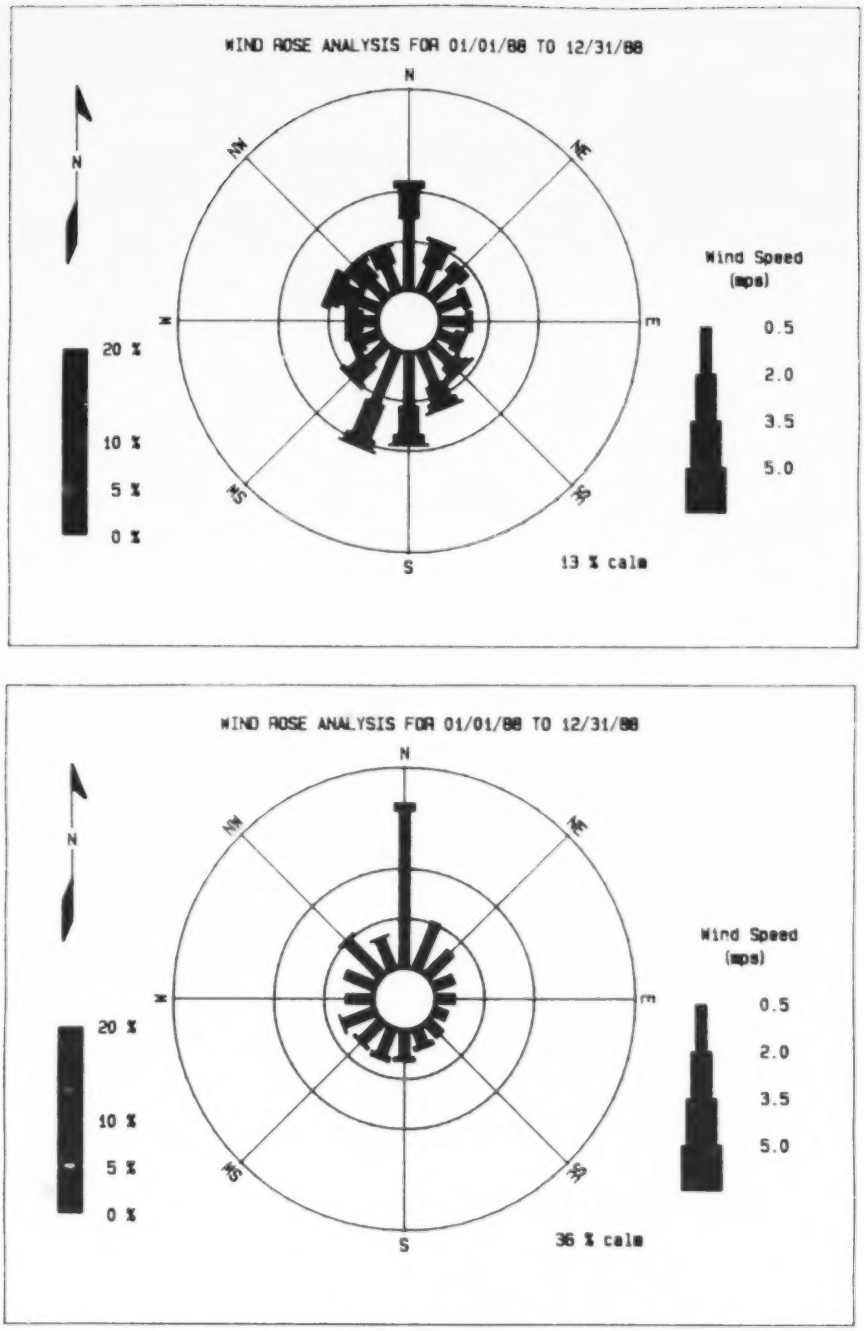


Figure 32. 1988 Wind rose for Site 101, Research Triangle Park, NC (A) and Site 102, Oak Ridge, TN (B)

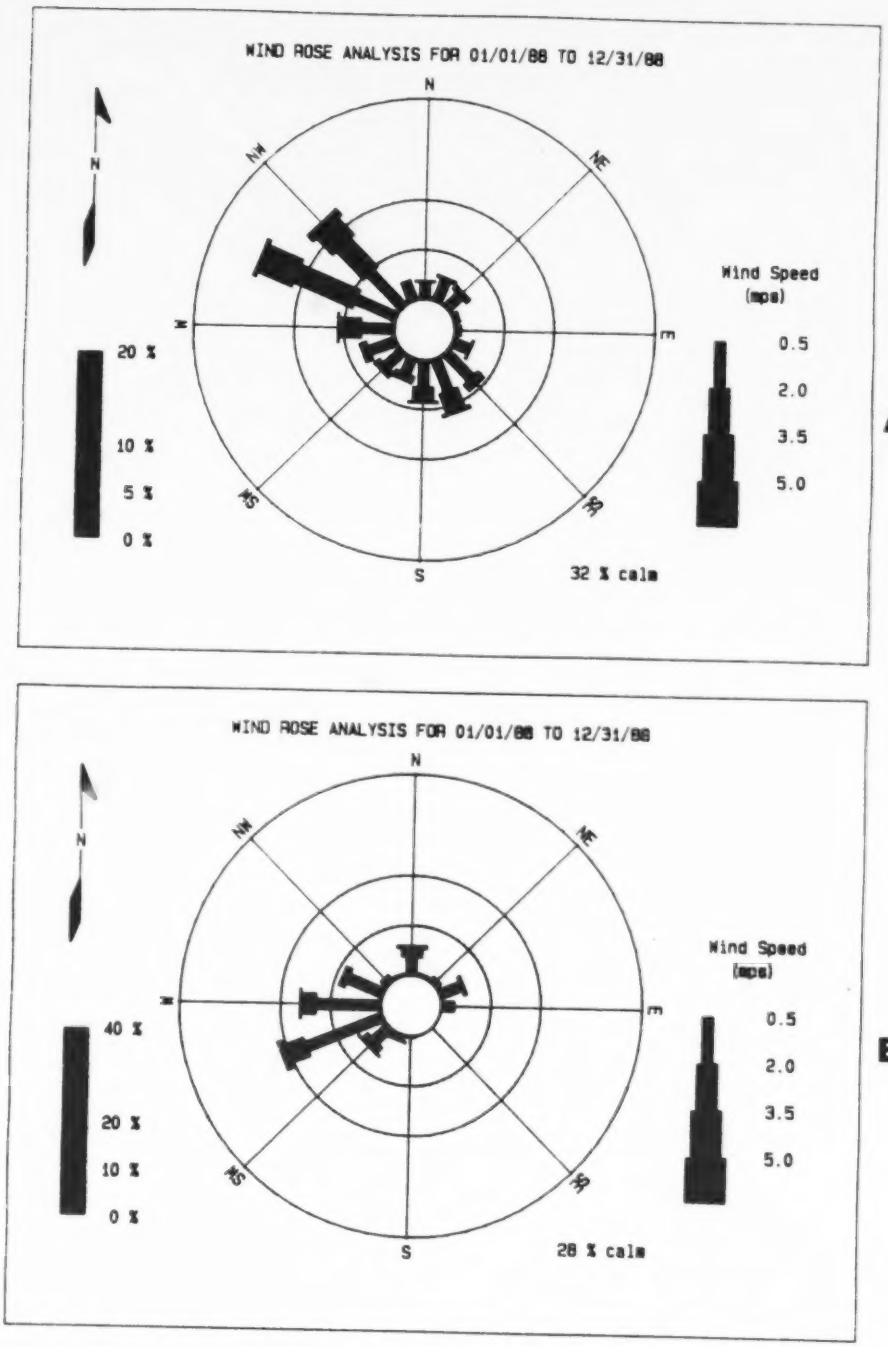


Figure 33. 1988 Wind rose for Site 103/4, West Point, NY (A) and Site 105, Whiteface Mountain, NY (B)

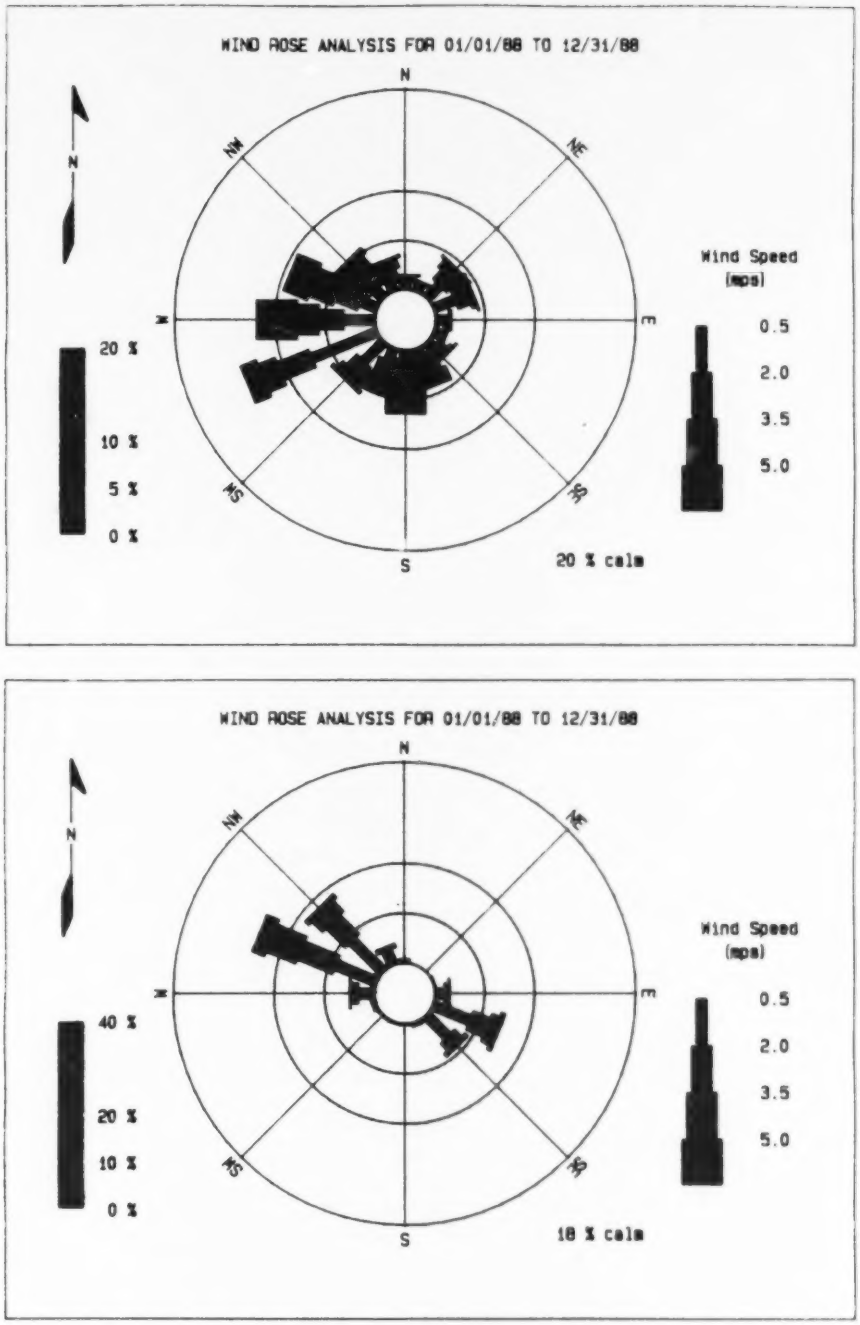


Figure 34. 1988 Wind rose for Site 106, State College, PA (A) and Site 107, Parsons, WV (B)

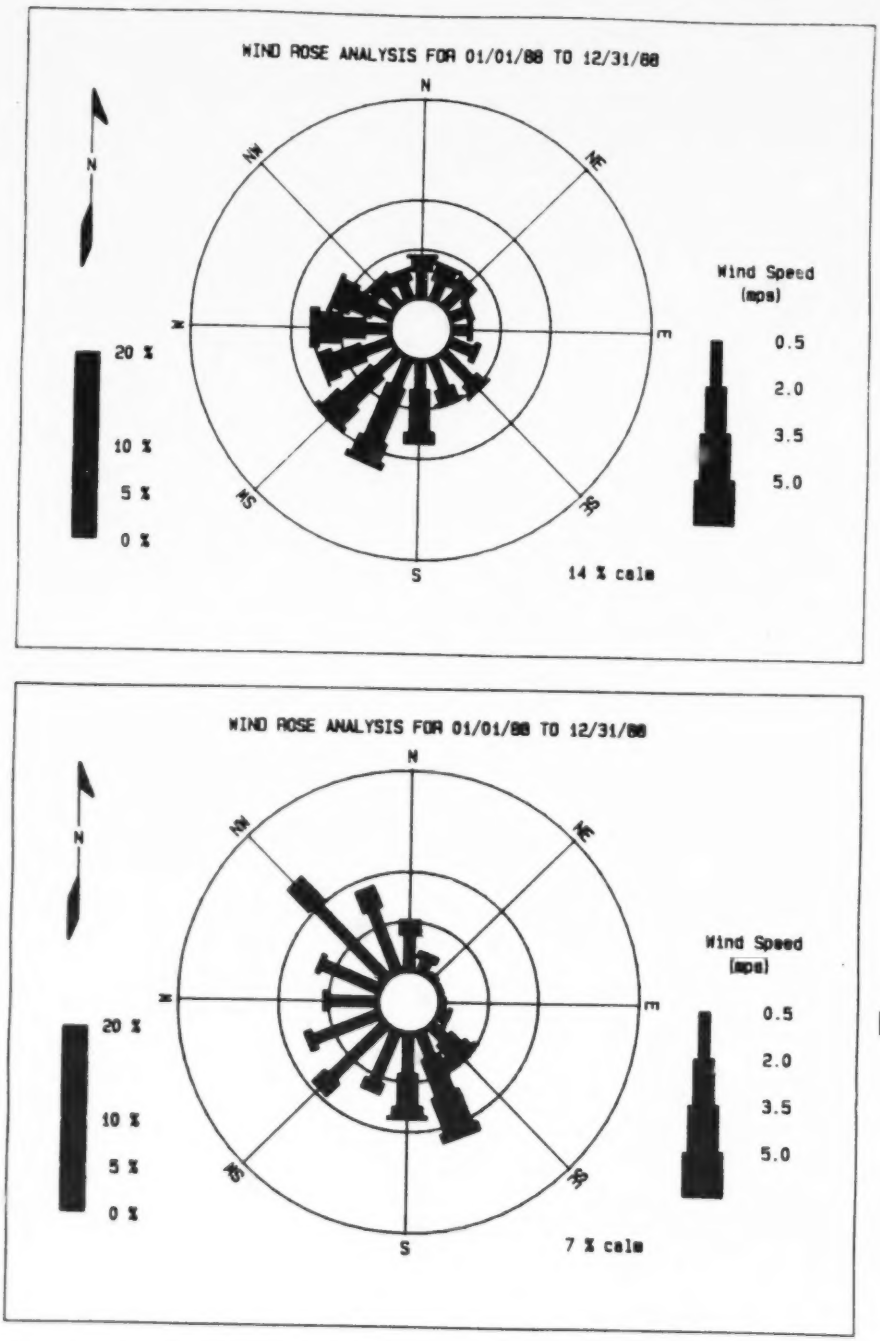
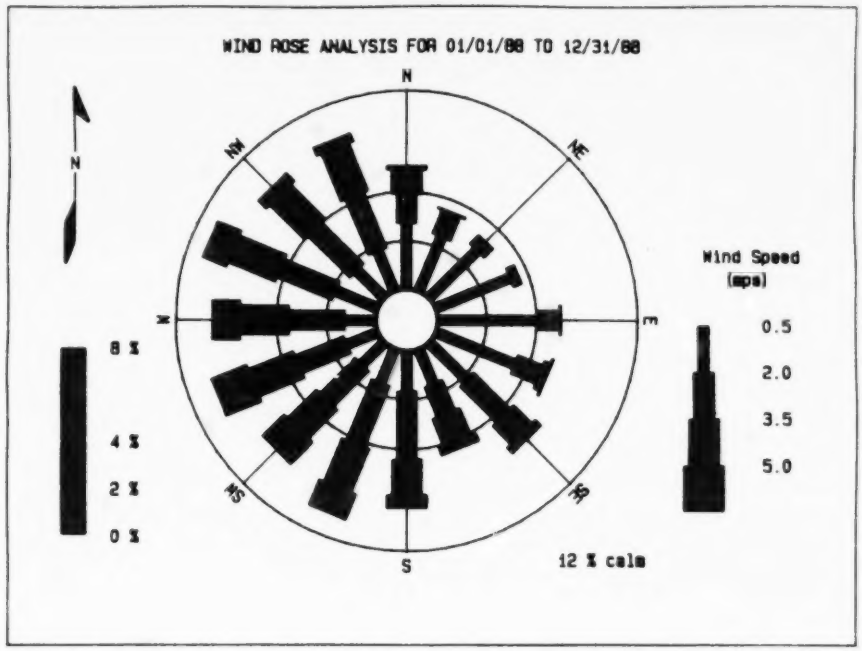
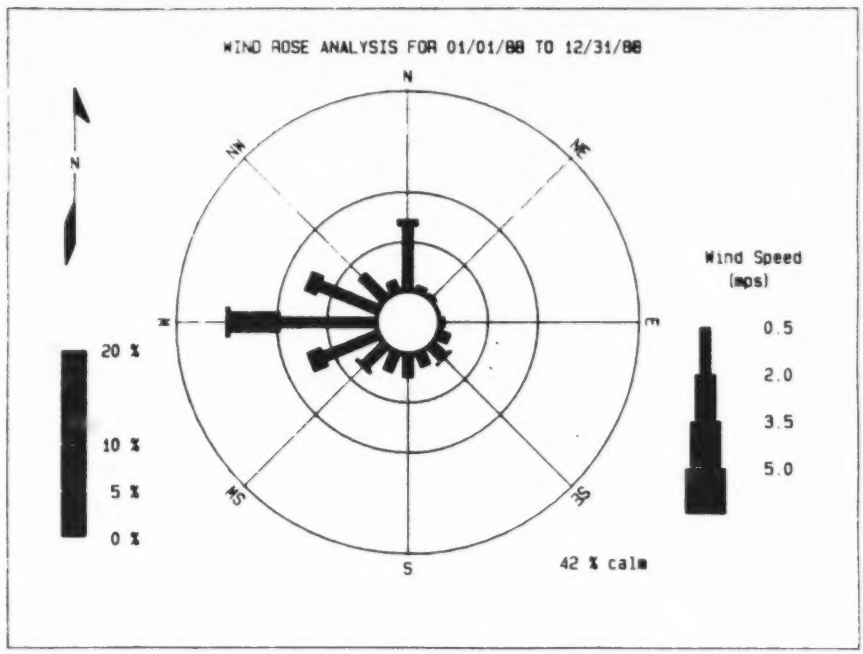


Figure 35. 1988 Wind rose for Site 108, Prince Edward, VA (A) and Site 110, Connecticut Hill, NY (B)

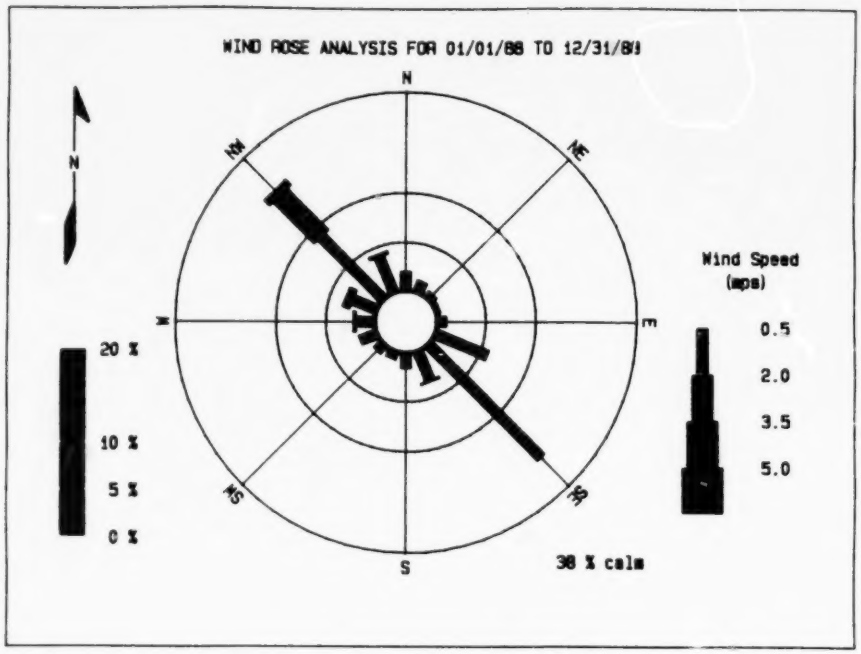


A

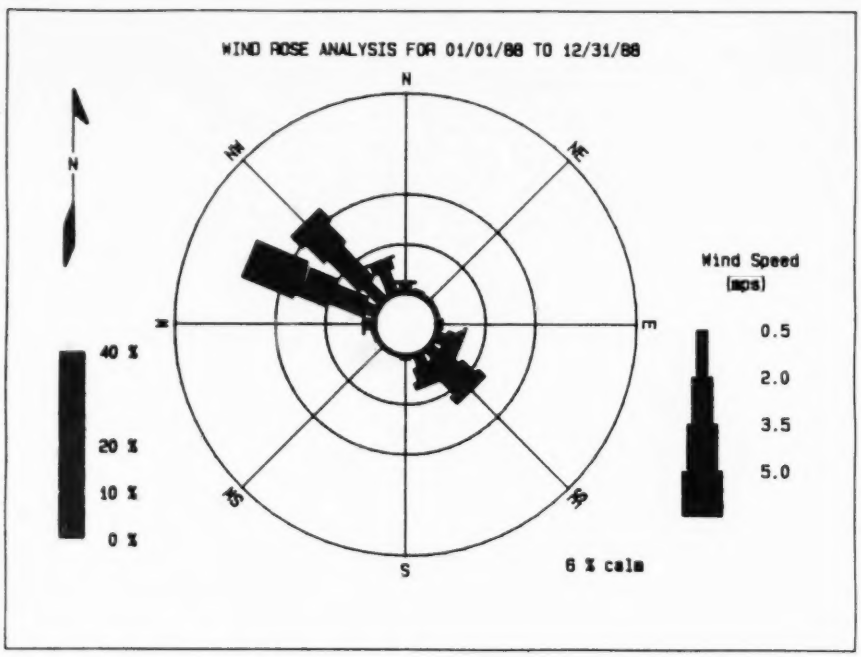


B

Figure 36. 1988 Wind rose for Site 113, M.K. Goddard, PA (A) and Site 117, Laurel Hill, PA (B)



A



B

Figure 37. 1988 Wind rose for Site 119, Cedar Creek, WV (A) and Site 120, Horton Station, VA (B)

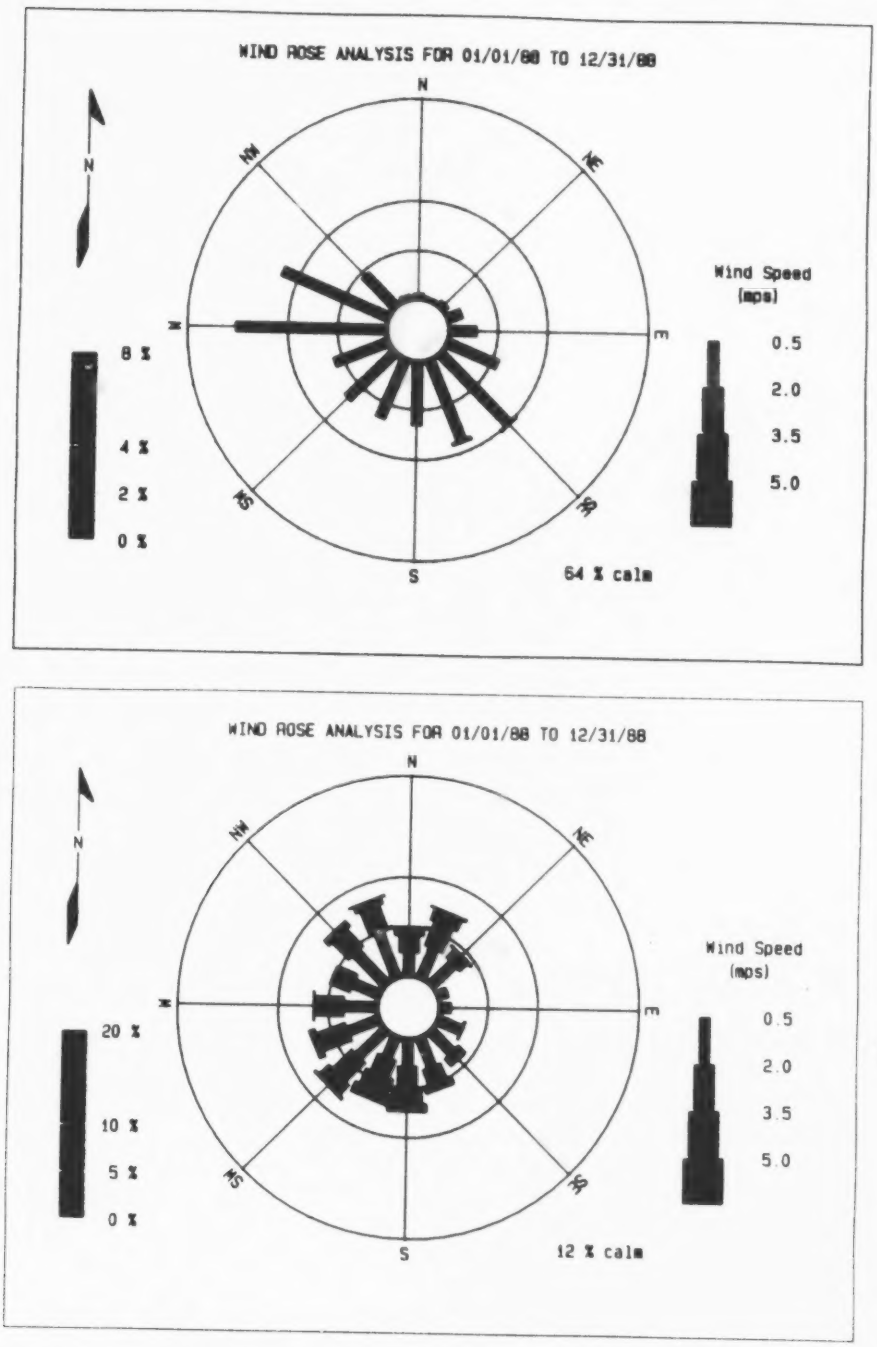


Figure 38. 1988 Wind rose for Site 121, Lilley Cornett Woods, KY (A) and Site 122, Oxford, OH (B)

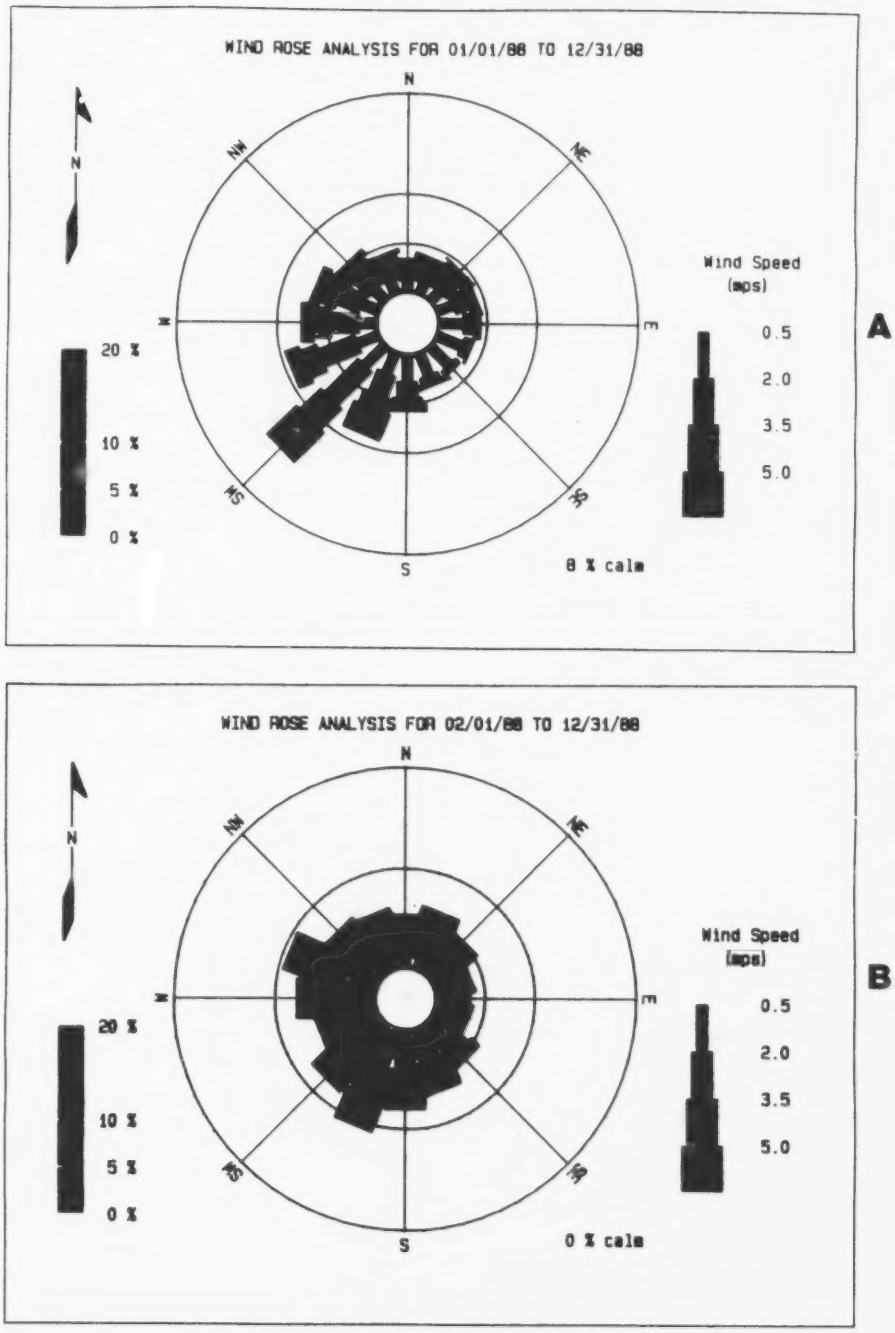


Figure 39. 1988 Wind rose for Site 129, Perryville, KY (A) and Site 130, Bondville, IL (B)

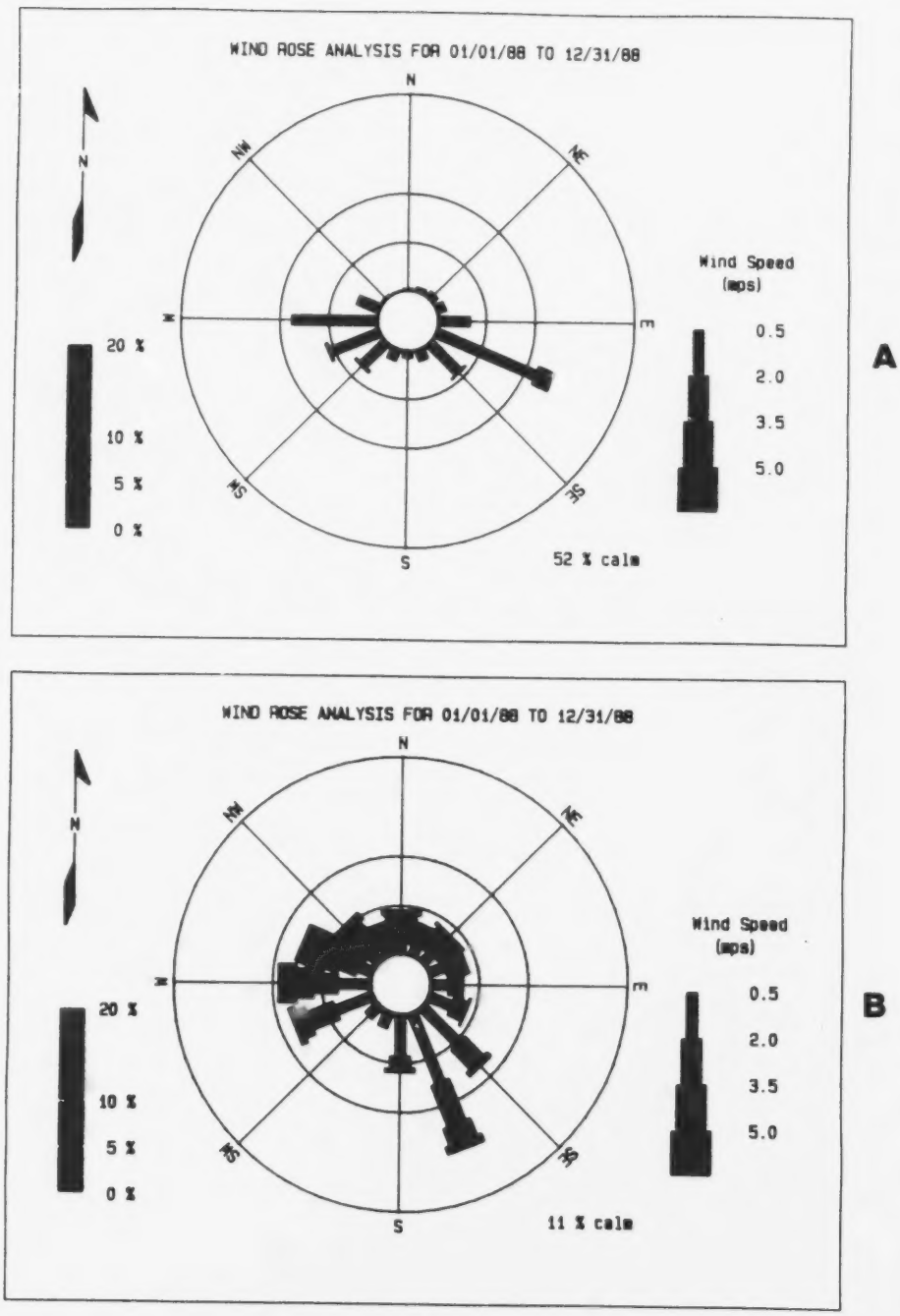


Figure 40. 1988 Wind rose for Site 137, Coweeta, NC (A) and Site 140, Vincennes, IN (B)

the same terrain classification and distinct differences between classifications. Results for the site in central Illinois (flat terrain) indicate a complete absence of calm periods and a nearly isotropic distribution of wind direction. Winds in all four speed categories are recorded in all 16 direction categories. Directional frequencies are greater than 10 percent only for one category (south-southwest) and less than 5 percent only for three categories (centered on east).

Wind characteristics in sites of rolling terrain are typified by data from central Kentucky (Site 129) and central Virginia (Site 108). Calm periods were recorded 8 percent and 14 percent of the time for these sites respectively, and there is a definite persistence of winds in the quadrant from south to west. The highest windspeeds are clearly associated with directional categories with high persistence.

Results for sites in complex terrain exhibit a high percentage of calm periods as well as fairly pronounced persistence in one or more directional categories. Results for the two sites in West Virginia (Sites 107 and 119) show distinctly bimodal distributions of wind direction. This is probably the result of terrain-induced circulation in the mountain valleys of the area. Data for the site in eastern Kentucky (Site 121) show the virtual absence of winds in the three highest speed classifications and the north-northwest, north, and north-northwest directional classifications.

Results for the mountaintop site in southwestern Virginia show relatively few calm periods but very high persistence. Winds are generally strong and persistent from the west-northwest and light and infrequent from the northeast, southwest, and adjoining directions. Winds in the north-northwest, northwest, and southeast directional categories account for more than 60 percent of the observations.

In general, the wind rose data support systematic differences in ventilation between sites in flat or rolling terrain and those in complex terrain. The latter thus appear to be meteorologically isolated from neighboring sites. This could account in part for the large spatial variability of SO_2 and HNO_3 along the flanks of the Appalachian Mountains.

4.4 ESTIMATED DRY DEPOSITION

The objective of NDDN, among other things, is to produce long-term data on patterns and trends of dry deposition across the continental United States. Ultimately, dry deposition rates will be calculated using one or more algorithms that couple land use or vegetation data, meteorological data, and air quality data to produce weekly, seasonal, and annual fluxes. This section presents estimation of dry deposition rates for 1988 using assumed values for annual average deposition velocity taken from the literature and annual average concentration data from 18 NDDN sites operational throughout 1988. Results are intended only to illustrate a possible range of dry deposition rates across the network. Results are specifically not intended to be an approximation of, or substitute for, deposition estimates based on the inferential approaches described by Hicks et al. (1985) and Wesely (1988).

The estimated deposition velocities used in these calculations are listed in Table 11. Tabulated values reflect a variety of theoretical estimates, experimental tests, and modeling results. Wu and Davidson (1988) used the resistance model of Hicks et al. (1985) to estimate weekly and annual deposition velocities of SO_2, SO_4^{-2}, and HNO_3 for three sites during 1986. Ranges of annual average deposition velocity for Oak Ridge, TN; Penn State University, PA; and Whiteface Mountain, NY (all current NDDN sites) were 0.07 to 0.13 centimeters per second (cm/sec) for SO_4^{-2}, 0.18 to 0.33 cm/sec for SO_2, and 0.96 to 1.9 cm/sec for HNO_3. Sheih et al. (1979) and Wesely and Lesht (1988) have developed computer routines for estimating deposition velocity as a function of land use, season, and meteorological stability class. Wesely and Lesht (1988) recently compared their model with a site-specific inferential technique similar to that which may be used for the NDDN (Hicks et al., 1988). Calculated deposition velocities were consistent with data shown in Table 11 and, on average, within ±30 to 40 percent of deposition velocities provided by the inferential technique. Little information is available on the deposition velocity for atmospheric NO_3^-. By analogy, the same range of deposition velocities was used for NO_3^- and SO_4^{-2}. However, differences in particle size and reactivity could result in substantial differences between these species.

Estimates of annual dry deposition for SO_4^{-2} plus SO_2 and for NO_3^- plus HNO_3 are shown in Figure 41. Values shown represent the mid-point of the estimated ranges of deposition and, therefore, are uncertain by at least ±50 percent. Estimated dry deposition for SO_4^{-2} plus SO_2 appears to be highest in southwestern Pennsylvania (Site 117) and eastern Tennessee (Site 102) and lowest in southwestern North Carolina (Site 137), northern New York (Site 105), and eastern Kentucky (Site 126). Not surprisingly, this pattern reflects the annual average SO_2 concentration, since in no case did SO_4^{-2} contribute more than 30 percent of the estimated dry deposition at any site. Relatively high deposition in northern Illinois, southern Indiana, and eastern Tennessee may be the result of local SO_2 emissions. Similarly high values in western Pennsylvania and West Virginia, on the other hand, seem to reflect more widespread sources.

Estimated dry deposition of NO_3^- plus HNO_3 shows similar values over much of the northeast and midwest but considerable variability in the vicinity of the Appalachian Mountains. Deposition at the mountaintop site in Virginia (Site 120) appears to be approximately three times that at complex terrain sites in eastern Kentucky and North Carolina (Site 121 and Site 137). The overall pattern is almost an exact transformation of annual HNO_3 concentration due to large differences in concentration and deposition velocity between HNO_3 and NO_3^-. At no site was NO_3^- responsible for more than 15 percent of the estimated dry deposition of NO_3^- plus HNO_3, and only at Site 146 (Argonne, IL) was NO_3^- responsible for more than 10 percent.

Wet and dry deposition data from a variety of NDDN sites are shown in Table 12. Wet deposition values (averaged over the 5-year period 1983 to 1987) were obtained from the National Atmospheric Deposition Program for all sites except Ithaca, NY. Data for this site, at the same time period, were obtained from quarterly data reports produced by the MAP3S program

TABLE 11. ESTIMATED DEPOSITION VELOCITIES FOR AEROSOLS AND GASES

Species	Vd (cm/s)	Reference
SO_4^{-2}	0.1 - 0.2	Sehmel, 1980; Sheih et al., 1979; Voldner et al., 1986; Wesely and Lesht, 1988; Wu and Davidson, 1988
NO_3^-	0.1 - 0.2	Assumed to be the same as SO_4^{-2}
SO_2	0.2 - 0.4	Sehmel, 1980; Sheih et al., 1979; Cadle et al., 1987; Wesely and Lesht, 1988; Wu and Davidson, 1988
HNO_3	1.0 - 2.0	Heubert, 1983; Wesely and Lesht, 1988; Wu and Davidson, 1988

Note: cm/s = centimeter per second
Vd = deposition velocity.

Source: Hunter/ESE, 1989.

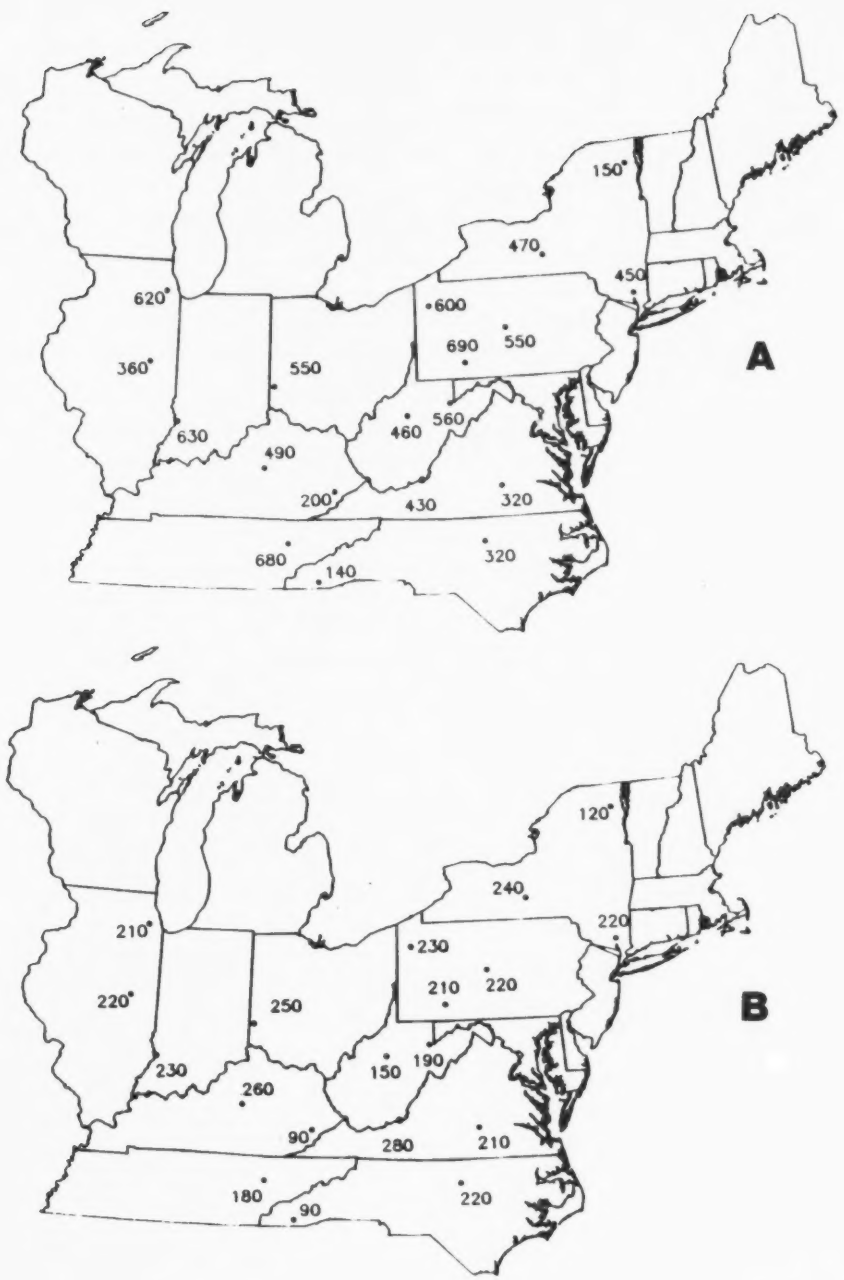


Figure 41. Estimated dry deposition of SO_4^{-2} plus SO_2 (A) and NO_3^- plus HNO_3 (B) (eg/ha) for 1988

TABLE 12. WET VERSUS DRY DEPOSITION AT SELECTED SITES

Site	Deposition (eq/ha-yr) SO_4^{-2} Wet*	SO_4^{-2} Dry+	NO_3^- Wet	NO_3^- Dry**
105 Whiteface, NY	390	100-200	230	100-200
110 Connecticut Hill, NY	490	310-630	310	190-380
106 Penn State, PA	720	360-730	350	180-370
107 Parsons, WV	850	370-730	360	170-340
122 Oxford, OH	560	360-730	220	200-400
130 Bondville, IL	550	240-470	220	180-340
129 Perryville, KY	470	330-670	190	180-350
101 Research Triangle Park, NC	340	210-420	160	140-290
102 Oak Ridge, TN	600	450-910	200	160-330

Note: eq/ha-yr = equivalents per hectare-year.

*Source of wet deposition data is National Atmospheric Deposition Program (IR-7)/National Trends Network, 1988.
+Sum of estimated dry deposition for SO_4^{-2} aerosol and SO_2.
**Sum of estimated dry deposition for NO_3^- aerosol and HNO_3.

Source: Hunter/ESE, 1989.

(M.T. Dana, personal communication, 1989). Again, the data tabulated for dry deposition reflect likely ranges for 1988 only. Results for sulfur deposition suggest that wet deposition is the dominant process in northern New York (Site 105), but that at most other sites, wet and dry deposition could be similar, especially if the upper limit for the deposition velocity of SO_2 is approached. Results for nitrogen suggest regional differences in the comparability of wet and dry deposition. For the northeast, dry deposition would be comparable to wet deposition only if the upper limit deposition velocity for HNO_3 is attained. Data for the midwest and southeast, in contrast, suggest that wet and dry deposition are comparable even if the lower limit deposition velocity for HNO_3 is attained.

4.5 OVERALL DATA QUALITY

As described in Section 2, extensive QC measures were undertaken to assure and document the overall quality of the NDDN database. This section provides a brief summary of NDDN QC data for 1988. Additional details on field and laboratory QC checks can be found in the quarterly data reports listed in the bibliography.

4.5.1 Field Data

Results of meteorological equipment calibrations performed during 1988 are summarized by quarter in Table 13. In general, calibration data show the majority of sensors were operating within accuracy requirements for the network. Temperature and relative humidity sensors typically responded within a few tenths and a few hundredths of a degree Celcius of NIST-traceable standards. Relative humidity, solar radiation, and rainfall amount responded within a few percent of calibration standards. Windspeed and wind direction were generally within ±0.2 m/sec and ±2 degrees of target values. Inspection of quarter to quarter variability for calibration data shows that all sensors, except relative humidity, responded consistently throughout the year. Data quality for relative humidity improved markedly from first quarter through fourth quarter due to adoption of a new sensor and the use of calibration salts in the field for adjustment of sensors.

Calibration data for continuous O_3 analyzers and MFC are presented in Table 14. O_3 and MFC calibrations were performed through the entire ambient air inlet to compensate for small ($\leq$3 percent) line losses and pressure drops within the system, respectively. In general, results for O_3 show that the instrument employed is highly stable and that it functioned with acceptable accuracy during the year. Aggregate errors for the network were within ±2 percent during each quarter, as represented by sensor versus transfer standard slopes, and errors for individual analyzers were invariably better than ±7 percent. Although occasional equipment failures occurred, no O_3 data were invalidated for lack of compliance with accuracy requirements.

MFCs also showed excellent stability, the errors tabulated in Table 10 indicate little instrumental drift between calibrations (i.e., from quarter

TABLE 13. SUMMARY OF METEOROLOGICAL SENSOR UNADJUSTED CALIBRATIONS DURING 1988

Quarter	Parameter Error (Site sensor minus transfer standard)						
	Temperature (°C)	Delta Temperature (°C)	Relative Humidity (%)	Solar Radiation (w/m^2)	Windspeed (m/sec)	Wind Direction (°)	Rainfall (%)
First							
Mean	0.10	-0.01	-1.1	-2.9	0.02	-0.2	-0.5
Standard Deviation	±0.11	±0.06	±10.2	±6.5	±0.12	±1.3	±4.0
Second							
Mean	-0.01	0.01	0.7	0.8	-0.01	-0.1	-0.6
Standard Deviation	±0.20	±0.05	±5.3	±2.7	±0.11	±1.8	±4.0
Third							
Mean	-0.04	0.01	0.6	1.2	0.01	-0.2	-0.4
Standard Deviation	±0.10	±0.03	±4.8	±4.5	±0.28	±2.6	±4.8
Fourth							
Mean	-0.03	0.01	0.2	0.4	-0.05	0.1	-0.3
Standard Deviation	±0.10	±0.04	±4.3	±4.9	±0.17	±1.6	±3.3

Note: °C = degrees Celsius.
° = degrees.
mm = millimeters
m/sec = meters per second.
w/m^2 = watts per square meter.

Source: Hunter/ESE, 1989.

TABLE 14. SUMMARY OF O_3 AND MASS FLOW CONTROLLER UNADJUSTED CALIBRATIONS DURING 1988

Quarter	O_3 Slope	O_3 Intercept	Filter Pack Flow (% error)*
First			
Mean	1.002	0.88	0.6
Standard Deviation	±0.012	±0.75	±3.9
Second			
Mean	0.993	0.14	0.7
Standard Deviation	±0.013	±0.76	±2.2
Third			
Mean	0.988	0.60	-1.1
Standard Deviation	±0.024	±1.15	±3.5
Fourth			
Mean	0.995	-0.17	-0.9
Standard Deviation	±0.019	±1.47	±2.2

Note: Slope and intercept are regression coefficients for calibration versus a NIST-traceable O_3 transfer standard.

*Error is calculated relative to the target flow of 1.50 Lpm.

Source: Hunter/ESE, 1989.

to quarter). Thus, the impact of uncertainties in flow on concentration calculations is expected to be minimal.

4.5.2 Laboratory Data

Laboratory accuracy and precision data from 1988 are summarized in Table 15. As described earlier, an NIST reference (2694-II) is analyzed once per analytical batch, a calibration verification standard (CVS) is analyzed after every tenth environmental sample, and 10-percent blind replicates are analyzed on different dates. Replicate analyses for Teflon® filters were discontinued in third quarter 1988 due to insufficient volumes after cation analyses.

Results for the NIST-reference material show that for each filter type and for each quarter instrumental error was less than or equal to 2.5 percent. During most quarters, it was much less than this, however. For example, mean recoveries during fourth quarter ranged from 100.5 ±1.3 percent for nylon SO_4^{-2} to 99.8 ±1.1 percent for Teflon® NO_3^-. CVS recoveries show similar results and indicate that instrumental drift was almost invariably less than 5 percent for each analytical run.

Results of replicate analyses show that, on average, the between-run precision for all analytes is less than 5 percent. However, there is considerable scatter in the replicate analyses, as reflected in the standard deviations for each analyte. This scatter is due primarily to the selection of field and laboratory blanks in the blind replication process. Blanks comprised more than 15 percent of the replicate analyses performed during 1988. For these samples, even a small increase or decrease in concentration propagates into a large percent difference between replicates. This is especially true if one analysis was less than the instrumental detection limit and the other was at or above the detection limit. In general, mass recoveries from replicate analyses differed by 1.0 μg/filter or less for each analyte. Given a typical sample volume of 7.5 m^3, this translates into a mean laboratory precision of approximately 0.15 $\mu g/m^3$ for SO_4^{-2}, NO_3^-, and HNO_3 and 0.2 $\mu g/m^3$ for SO_2.

Laboratory accuracy and precision should not be confused with overall sampling accuracy and precision. The accuracy of the NDDN filter pack sampling approach is unknown and its precision should be determined based on collocated field sampling, rather than laboratory replicates. Nevertheless, the results in Table 15 show that laboratory operations conform with accuracy and precision requirements for this project.

Results of collocated field monitoring during 1988 are shown in Table 16 (continuous sensors) and Table 17 (filter packs). Temperature and delta temperature data indicate that, on average, measurements are within 0.1°C and that only rarely do differences exceed ±0.2°C, the manufacturer's specification for the equipment. Relative humidity data exceeded the precision goal of ±10 percent during first quarter 1988 but showed marked improvement in subsequent quarters. Although both sensors passed calibration checks late in the first quarter, the collocated sensor was found to have a dirty inlet. This inlet caused the collocated sensor to

TABLE 15. SUMMARY OF LABORATORY ACCURACY AND PRECISION DURING 1988

Quarter	QC Check	Filter Type/Analyte					
		Teflon®		Nylon		Whatman	
		SO_4^{-2}	NO_3^-	SO_4^{-2}	NO_3^-	SO_4^{-2}	NO_3^-
First	NIST Recovery*	102.5 ±2.2	100.2 ±0.9	101.9 ±2.0	99.6 ±1.0	98.9 ±1.2	100.7 ±1.6
	CVS Recovery+	99.0 ±1.4	99.8 ±0.9	99.5 ±1.4	99.5 ±1.2	98.5 ±1.4	99.3 ±1.9
	Replicates**	4.1 ±12.6	4.8 ±3.0	3.6 ±8.8	2.5 ±9.1	0.7 ±5.8	30.3 ±34.8
Second	NIST Recovery*	99.2 ±1.5	99.8 ±1.4	99.1 ±1.4	99.6 ±0.9	98.9 ±1.0	99.8 ±0.9
	CVS Recovery+	99.7 ±1.3	99.8 ±1.5	100.3 ±1.2	100.0 ±1.4	99.0 ±1.2	98.9 ±1.3
	Replicates**	1.3 ±11.5	3.6 ±11.3	1.5 ±5.4	0.8 ±9.2	0.9 ±5.3	0.1 ±4.9
Third	NIST Recovery*	99.6 ±1.5	99.4 ±1.3	99.8 ±1.4	100.4 ±1.3	100.3 ±1.6	99.8 ±1.9
	CVS Recovery+	99.2 ±1.4	9.8 ±5.7	99.0 ±1.4	100.8 ±2.7	98.6 ±1.3	99.3 ±1.4
	Replicates**	NA	NA	1.5 ±12.5	1.0 ±10.1	1.2 ±14.8	0.4 ±9.9
Fourth	NIST Recovery*	100.3 ±1.0	99.8 ±1.1	100.5 ±1.3	100.2 ±1.2	100.5 ±0.8	100.4 ±0.9
	CVS Recovery+	98.9 ±0.9	99.1 ±1.0	98.8 ±4.5	99.6 ±1.0	99.5 ±1.0	99.8 ±1.2
	Replicates**	NA	NA	2.0 ±5.3	2.1 ±5.6	2.5 ±16.8	0.3 ±11.4

Note: CVS = continuing verification standard.
NA = not applicable.
NIST = National Institute of Standards and Technology.

*Mean percent recovery of NIST SRM 2694-II.
+Mean percent recovery of an independent continuing verification standard analyzed after every tenth sample.
**Mean percent difference for duplicate sample analyses performed on different dates.

Source: Hunter/ESE, 1989.

TABLE 16. PRECISION DATA FOR COLLOCATED CONTINUOUS SENSORS LOCATED AT WEST POINT, NY DURING 1988

Quarter	Difference of 24-Hour Averages (i.e., Site 103 - Site 104)							
	Temperature (°C)	Delta Temperature (°C)	Relative Humidity (%)	Solar Radiation (W/m^2)	O_3 (ppb)	Windspeed (m/sec)	Wind Direction (°)	Sigma Theta (°)
First								
Mean	-0.07	-0.01	-11.0	-2.4	-0.02	-0.01	1.8	-6.5
Standard Deviation	±0.05	±0.06	±6.7	±2.9	±0.8	±0.23	±5.9	±5.4
Second								
Mean	-0.04	0.04	-1.1	-3.5	0.28	0.10	1.7	-10.1
Standard Deviation	±0.06	±0.07	±1.4	±3.7	±0.7	±0.26	±10.9	±9.3
Third								
Mean	0.00	-0.06	-3.5	-2.8	0.76	0.04	2.7	-6.9
Standard Deviation	±0.06	±0.08	±0.23	±2.6	±0.8	0.17	±6.2	±6.6
Fourth								
Mean	NP	NP	NP	NP	NP	NP	NP	NP
Standard Deviation	NP	NP	NP	NP	NP	NP	NP	NP

Note: °C = degrees Celsius.
° = degrees.
mm = millimeters
m/sec = meters per second.
NP = not performed.
ppb = parts per billion.

Source: Hunter/ESE, 1989.

TABLE 17. PRECISION DATA FOR COLLOCATED FILTER PACK SAMPLING AT WEST POINT, NY DURING 1988

Quarter	Statistic	Analyte			
		SO_4^{-2}	NO_3	HNO_3	SO_2
First	$\bar{X}$ ($\mu g/m^3$)	4.06	1.09	2.52	19.0
	$\bar{D}$ ($\mu g/m^3$)	-0.11	-0.02	0.10	0.2
	PD (%)	-2.7	-1.8	4.0	1.1
	MAPD (%)	2.3	10.1	5.0	3.7
Second	$\bar{X}$	5.74	0.48	2.94	10.1
	$\bar{D}$	-0.11	0.08	0.15	0.06
	PD	-1.8	16.7	5.1	0.6
	MAPD	2.8	27.9	5.4	2.4
Third	$\bar{X}$	8.81	0.23	3.23	8.39
	$\bar{D}$	-0.11	0.04	0.71	-0.05
	PD	-1.2	17.4	22.0	-0.6
	MAPD	4.6	30.9	18.3	4.8
Fourth	NP	NP	NP	NP	NP

Note: $\bar{X}$ = mean concentration for both samplers during the quarter.
$\bar{D}$ = mean difference between samplers during the quarter.
PD = percent differences of the quarterly means.
MAPD = mean absolute percent difference between weekly samples.
NP = not performed.

Source: Hunter/ESE, 1989.

take longer than the primary sensor to dry out after a period of high relative humidity (i.e., ≥95 percent). After cleaning, the two sensors responded much more coherently, as reflected in the data for second and third quarter. Collocated O^3 data show that differences between analyzers were on average within 1 ppb and rarely exceeded 2 ppb.

Data for solar radiation, windspeed, and wind direction meet precision goals; however, data for wind direction show much more variability than can be explained by the expected measurement errors. Although there is no precision goal for sigma theta, results for this parameter also show more scatter than was initially expected. One explanation for these observations is terrain effects. The site is located in a narrow valley within an area of complex terrain. In contrast, recent data for a collocated site in rolling terrain (Site 153--Georgia Station, GA) exhibit precision of 1.0 degrees, or less, for both wind direction and sigma theta.

Results of the collocated filter pack sampling at West Point, NY show that precision data for SO_4^{-2} and SO_2 invariably meet the project objective of ±5 percent. Percent differences based on quarterly average concentrations are well below 5.0 (typically below 2.0), while mean absolute percent differences based on weekly samples range from 2.3 to 4.8. There is no evidence of a relationship between concentration and precision, as reflected by relatively constant percent differences from quarter to quarter.

Results for NO_3^- show that differences between quarterly average concentrations are less than 0.1 $\mu g/m^3$, but that percent differences for a quarter or for individual samples can be quite large. As illustrated in Figure 42, NO_3^- data show appreciable scatter over the range of observed concentrations and generally much more scatter than the other chemical parameters. HNO_3 data show concentration differences with ±0.2 $\mu g/m^3$ and percent differences of 5.4 or less for the first and second quarters but a significant deterioration in precision during the third quarter. Clearly, differences in NO_3^- cannot explain differences in HNO_3 during third quarter and, therefore, the total NO_3^- collected by the two samples differed appreciably. These differences rule out some but not all of the artifact reactions that can occur within the filter pack system. The occurrence of an undetected leak or a systematic breakthrough of HNO_3 in one of the systems is currently being investigated. In any event, collocated data at the same site for previous quarters and other sites for subsequent quarters suggest that the third quarter 1988 precision data for HNO_3 are anomalous.

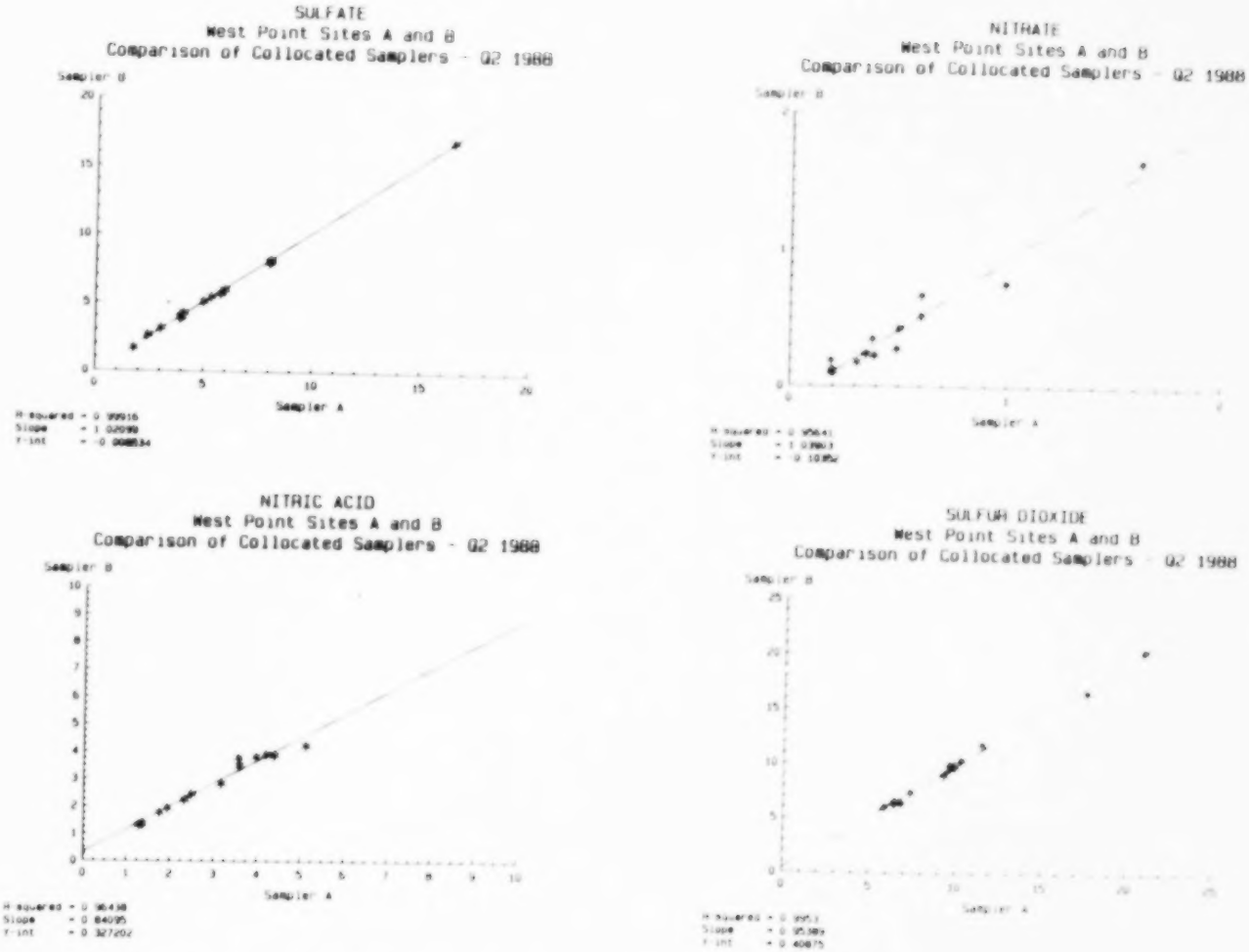


Figure 42. Scatter plots of collocated filter pack data from Site 103/4, West Point, NY--second quarter 1988

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